# MAGNETIC ROTATION SPECTRA OF MOLECULES

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OF MOLECULES

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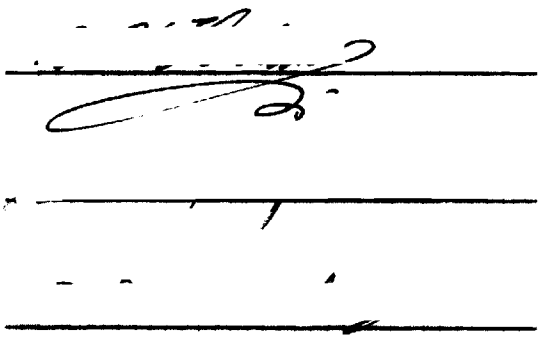

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# TABLE OF CONTENTS

# LIST OF TABLES

# LIST OF ILLUSTRATIONS

LIST OF ILLUSTRATIONS
(Continued)

## SUMMARY

Although the magnetic rotation spectrum of a gas has been known since 1906, it has only been studied for a very few molecules. From 1906 to 1914, R. W. Wood and his associates investigated the magnetic rotation spectra of $Na_2$ and $I_2$, and reported the experimental measurements of the band systems without any theoretical explanation. Later, from 1928 to 1934, F. W. Loomis and his associates extended the investigation to different alkali molecules, and found that magnetic rotation spectra can be utilized to extend vibrational analyses of absorption bands of these molecules and thus to estimate accurately the heats of dissociation. It is the purpose of the present investigation to study the details of the magnetic rotation spectra of diatomic halogen and interhalogen molecules.

A magnetic rotation spectrum can be described in the following way. White light is sent through two crossed Nicol prisms, between which is placed an optical cell or absorption tube, filled with the vapor of a compound to be studied. The compound is assumed to be not naturally optically active, or the experiment has to be suitably modified. As long as there is no magnetic field along the tube, no light goes through the system. However, when a longitudinal magnetic field is applied, sometimes a small part of the light does go through -- namely, that part of the light whose plane of polarization has been rotated. A spectrum of this transmitted light is known as the magnetic rotation spectrum of the compound.

The present investigation has been undertaken with the expectation that the magnetic rotation spectrum of a gas could be utilized to supply some valuable information which will aid the analysis of its absorption spectrum. In absorption spectroscopy, electronic transitions of a molecule generally occur in the ultra-violet and visible regions but frequently they overlap each other so much that it is difficult to carry out the analysis. However, only a few of these electronic transitions will appear in the magnetic rotation spectrum, and for each transition only a few lines will be present instead of a whole band of numerous lines. Hence a magnetic rotation spectrum is much simpler than the absorption spectrum.

Some theoretical studies on the magnetic rotation spectra of molecules have been made by L. Rosenfeld, R. de L. Kronig, R. Serber and T. Carroll. An extension of their discussion to diatomic halogen and interhalogen molecules has been carried out in the present investigation. The results on diatomic molecules may be summarized as follows: strong magnetic rotation spectra are expected for electronic transitions in which a change in magnetic moment along the direction perpendicular to the internuclear axis takes place. Thus transitions of the types $^1\Pi - {}^1\Sigma$, $^3\Pi_1 - {}^1\Sigma$, $^3\Sigma - {}^1\Sigma$ and $^2\Sigma - {}^2\Sigma$ (in weak field) are expected to give magnetic rotation spectra, while no strong transitions are predicted for $^1\Sigma - {}^1\Sigma$, $^3\Pi_0 - {}^1\Sigma$ and $^2\Sigma - {}^2\Sigma$ (in strong field). Weak transitions occur in violation of these predictions, if rotational distortion or other perturbations cause mixing of non-magnetic levels with nearby magnetic levels.

Apparatus for the experimental study of the magnetic rotation spectra of molecules was set up using the Western Union Concentrated-Arc

as a light source. The light was passed through a colimating lens, a polarizer, a 40 cm optical cell, and an analyzer. It was then focused onto the slit of a spectrograph by means of a combination of concave spherical and cylindrical lens. Two Ahrens prisms were employed as the polarizer and analyzer, and the three-meter replica-grating spectrograph of the Jarrell-Ash Company was used to photograph a spectrum on 35 mm film. The longitudinal magnetic field was supplied by an electromagnet of about 1000 gauss.

A search for magnetic rotation spectra of ICl, IBr and $Br_2$ was made in the near-infrared, visible and ultra-violet regions. During the course of analyzing these spectra, it was found necessary to study the isotopic species $IBr^{79}$, $IBr^{81}$, $Br^{79}Br^{79}$ and $Br^{81}Br^{81}$. These isotopic species were prepared from $AgBr^{79}$ and $AgBr^{81}$ which were loaned to us by the Atomic Energy Commission. The silver bromide was oxidized into bromine by potassium dichromate in sulfuric acid solution and iodine monobromide was prepared by mixing equal moles of iodine and bromine in the absorption cell.

Experimental results showed close agreement of the general features with the conclusions drawn from the theoretical study. Because of the magnetic upper state of the transition $^3\Pi_1 - {}^1\Sigma^+$, ICl was found to give a magnetic rotation spectrum in the visible region which consists of many sharp bright lines corresponding to the band origins of its absorption spectrum. However, IBr gives only a magnetic rotation spectrum for the transition $0^+ - {}^1\Sigma^+$ where the upper state $0^+$ appears to be perturbed by a magnetic state such as $1({}^1\Pi)$. The magnetic rotation spectrum of $Br_2$ corresponding to the transition $^3\Pi_{0_u^+} - {}^1\Sigma_g^+$ may be attributed to

rotational distortion analogous to that observed in $I_2$.

A search for magnetic rotation spectra in the near-infrared region failed to reveal any positive results for IBr and $Br_2$. Their absorption spectra in this region are diffuse and have been assigned to the transition $^3\Pi_1 - {}^1\Sigma^+$. This absence of magnetic rotation spectra might be explained by either the diffuseness of the absorption spectra or the wrong assignment of the transition. Their weak absorption spectra in this region might be due to a forbidden transition like $0^-(^3\Pi) - {}^1\Sigma^+$.

Between 5770A and 6682A, ICl gives a strong magnetic rotation spectrum of many lines most of which can be identified with the corresponding band origins in the absorption spectra of $ICl^{35}$ and $ICl^{37}$ for the transition $^3\Pi_1 - {}^1\Sigma^+$. Since the iodine monochloride prepared from natural chlorine actually consists of two isotopic species $ICl^{35}$ and $ICl^{37}$ in the ratio of three to one, the lines ascribed to $ICl^{35}$ were observed to be approximately three times as intense as those ascribed to $ICl^{37}$. Other lines are believed to be present because the upper state $^3\Pi_1$ is perturbed with a repulsive state such as $0^-(^3\Pi)$ which acquires magnetic properties through rotational distortion. This pertubation is actually indicated by the sudden diminution of the intensity of the magnetic rotation lines after $v' = 28$ at 5813.8A for both isotopic species, and is substantiated by the anomalous magnitude of the $\Delta G'$ value between $v' = 28$ and $v' = 29$ and the deviation from linearity of the $\Delta G'$ vs $v'$ curve in this region. From the magnetic rotation of ICl, vibrational isotopic shifts were measured nearly to the dissociation limit and found to be in good agreement with values calculated from the vibrational spacing.

Iodine monobromide gives a magnetic rotation spectrum of three separate bands between 5517A and 5710A for the transition $0^+ - {}^1\Sigma^+$. The perturbation of the upper state $0^+$ with a magnetic state such as ${}^1\pi$ is believed to be responsible for the appearance of this magnetic rotation spectrum. Upon close examination of the individual magnetic rotation spectra of $IBr^{79}$ and $IBr^{81}$, it was found that the points of perturbation are concentrated in the vibrational bands $v' = 25$ for $IBr^{81}$ and $v' = 26$ for $IBr^{79}$ and that the three distinct bands arise from the vibrational levels $v'' = 0$, 1 and 2 respectively of the ground electronic state.

Between 5110A and 5370A, the absorption and magnetic rotation spectra of bromine from natural sources appear to be very complex, because the spectra of the three isotopic species $Br^{79}Br^{79}$, $Br^{79}Br^{81}$ and $Br^{81}Br^{81}$ in natural bromine overlap each other. From the investigation of the spectra of the individual isotopic species $Br^{79}Br^{79}$ and $Br^{81}Br^{81}$, it was found that both of these species give the same correlation between the absorption and magnetic rotation spectra: that is, absent or weak lines at low J values and strong lines at high J values. This correlation agrees very well with the theoretical study on the assumption that the magnetic rotation spectra of the isotopic species of bromine are due to the rotational distortion in the upper state ${}^3\pi_{0_u^+}$.

During the study of the magnetic rotation spectra of bromine, several peculiar phenomena were observed which led to studies of the effects of changes of temperature and pressure and the presence of foreign gases. The results can be summarized in two statements. First, raising either the temperature or pressure of bromine in the cell increases the actual number of molecules of bromine in $v'' = 1$, 2, etc.,

and thus increases the absorption in the green region due to the intense continuous spectra from these vibrational levels. This increase in absorption decreases the intensity of the magnetic rotation spectrum very rapidly. Secondly, increasing the vapor pressure of bromine to 50 mm and higher or introducing foreign gases like He and A enhances the rate of collisions among the molecules. These collisions relax the selection rule of $g \not\leftrightarrow u$ on perturbation and cause a mixing of the upper state $^3\Pi_{0_u^+}$ with a repulsive state $0_g^+$. This pertubation results in an induced predissociation of bromine and hence destroys its magnetic rotation spectra.

# CHAPTER I

## INTRODUCTION

Detailed information about the structure of a molecule (diatomic or polyatomic) can usually be found from its absorption spectra. The latter can be classified according to the frequencies of absorbed radiation or according to the origin of spectra: namely, the microwave spectrum is due to rotational transitions; the infrared spectrum is due to vibrational transitions; and the visible and ultra-violet spectrum is due to electronic transitions. Although numerous data have been collected and many theories have been developed for explanations and interpretations, the whole problem of absorption spectroscopy is far from complete.

Since electronic transitions are of particular interest here, no further discussion will be made of pure vibrational and rotational transitions. In general a molecule has many different electronic states, which can be characterized by such properties as the multiplicity and symmetry of the wave-functions describing the states. The intensity of optical transitions between electronic states is governed by selection rules, which can be obtained by evaluating the matrix elements of the electric dipole moment between the electronic states involved. The most general selection rules for both diatomic and polyatomic molecules are those based on multiplicity and symmetry.

Electronic transitions can be further subdivided into two groups, the so-called "allowed" and "forbidden" transitions. Allowed transi-

tions are those which obey the selection rules, while forbidden transitions are those which contradict the selection rules. Forbidden transitions can be observed by using very long absorbing paths (considerably longer than are necessary for the allowed transitions). The occurrence of forbidden transitions may be due to one or more of the following reasons: (1) the selection rule that is violated may hold only to a first approximation; (2) the selection rule may hold strictly for dipole radiation but not for quadrupole radiation or magnetic dipole radiation; and (3) the selection rule may hold only for the completely free and uninfluenced molecules and may be violated in the presence of external fields, collisions with other molecules, and the like (enforced dipole radiation). Among these reasons, the first is of special interest for ordinary electric dipole radiation.

The selection rule on multiplicity (delta S = 0) is valid only to the first approximation. It holds less and less strictly with increasing spin-orbit interaction: that is, with increasing atomic number. Thus for molecules containing heavy atoms, the singlet-triplet transitions (delta S $\neq$ 0) may represent fairly intense absorption bands.

When a polyatomic molecule starts to vibrate, the selection rule on the symmetry of the electronic states may be relaxed. The excitation of vibrations pertrubs the nuclear symmetry of the molecule and causes mixing of the electronic wave-function with the wave-functions of energetically neighboring states. Such mixing may make possible transitions to vibrating states of the excited electronic state whereas a transition to the nonvibrating state is forbidden. This kind of transition is called a "vibronic" transition. It is not directly connected

with the present investigation, and so will not be discussed any further.

The main purpose of this investigation is to study the singlet-triplet transitions of diatomic and polyatomic molecules. These transitions are not usually detected by ordinary absorption spectra of allowed transitions and consequently, as most molecules have a singlet ground state, the properties of triplet electronic states can not usually be derived from their absorption spectra. Some special techniques have to be developed in order to study these triplet states. One of the techniques which seems to be very promising is the study of the so-called "magnetic rotation spectra" of molecules.

Experimentally, the magnetic rotation spectrum of a molecule can be observed in the following way. White light is sent through two crossed Nicol prisms, between which is placed a tube (or optical cell) filled with the vapor of a certain compound. As long as there is no magnetic field, no light passes through the system. However, when a longitudinal magnetic field is applied, a small part of the light does go through -- namely, that part for which the plane of polarization has been rotated. This rotation of the plane of polarization occurs to a large extent only near an absorption line of the compound which shows an appreciable Zeeman effect. All singlet-triplet transitions should show Zeeman effect, and are thus expected to give magnetic rotation spectra.

Since the molecules $I_2$, $Br_2$, IBr, and ICl are known to have a high degree of spin-orbit interaction, singlet-triplet transitions will appear in their absorption spectra due to the relaxation of the selection rule on multiplicity. These transitions are expected to give magnetic rotation spectra. Actually the green magnetic rotation spectra of $I_2$

and $Br_2$ were first observed by Rhigi in 1898 and later photographed by Wood in 1914. During the course of the present investigation, magnetic rotation spectra of IBr and ICl were observed and photographed for the first time. A detailed study of the magnetic rotation spectra of these molecules should pave the way for the study of singlet-triplet transitions of polyatomic molecules such as $SO_2$, $CS_2$, and others.

It has been found that the molecule, $NO_2$, gives an intense magnetic rotation spectrum in the whole visible region. This molecule has a doublet ground state which is sensitive to a magnetic field. An explanation of the occurrence of this magnetic rotation spectrum will be attempted elsewhere in this thesis.

From the study of magnetic rotation spectra of diatomic and polyatomic molecules, the properties of triplet electronic states can be found. These triplet states are important in the understanding of molecular structures of molecules.

# CHAPTER II

## REVIEW OF LITERATURE

When plane-polarized light is sent through a solid, liquid, or gas in a direction parallel to the applied magnetic field, the plane of polarization is rotated. This phenomenon is called the Faraday effect. The magnetic rotation spectrum may be considered as a special case of the Faraday effect; it is the Faraday effect on gaseous molecules when the incident plane-polarized light is near the absorption band of the molecule.

The Faraday effect is so named because it was Michael Faraday who discovered this effect in 1845 (1). Faraday believed that if two electric charges attract each other, the medium between two such charges is in a different state than it would be if the charges were not present; and, if so, such an altered state should be detectable by observing the alteration in some physical property of the medium. As early as 1822, he had experimented with a beam of polarized light passing through a transparent solution carrying a current, to see whether the current caused any "depolarizing" action. Although he repeated the experiment several times in subsequent years, the results were all negative. In 1845 he returned to the problem but still with negative results. He then tried solid dielectrics between plates of metal foil connected to a high voltage source to see whether, under electric stress, they would show any optical effects. The results were still negative.

Faraday then substituted a magnetic field for the electrostatic

field to see whether the former would cause any depolarizing action on the beam of light. Various substances were tried but still with negative results. Finally he placed in the magnetic field a very dense piece of lead glass which he had made many years earlier. When the magnetic lines were parallel to the direction of the beam of polarized light, he observed that the plane of polarization was rotated.

Thus the phenomenon of rotating the plane of polarization by a transparent isotropic medium in a powerful magnetic field, when the light traverses the medium in the direction of the lines of magnetic force, is called the Faraday effect. If plane-polarized light is reflected back and forth through the same medium, the plane of vibration is found to rotate farther with each traversal. This is not the case for optically active substances like quartz, where upon one reflection the light emerges vibrating in the same plane in which it entered. It should be noted that when the field direction is reversed, the direction of rotation of the place of the incident light vibrations is also reversed. Therefore, the sense of the rotation is defined in terms of the direction of the field, positive rotation being that of a right-handed screw advancing in the direction of the field or that of the positive current in the coil which produces the field.

Shortly after the discovery by Michael Faraday, E. Becquerel (1820-1891) observed that the addition of salts of iron to water diminished the rotatory power which it acquired in a magnetic field, an experiment which Verdet interpreted as proving that the iron salts possessed a rotatory power of opposite sense from the exhibited by the diamagnetic substances investigated by Faraday. The latter he

called "positive rotation" (i.e., in the same direction as that of the current producing the field), as distinguished from the "negative rotation shown by paramagnetic substances. But it was presently found that titanium tetrachloride, though diamagnetic, exhibited a "negative" rotation, a circumstance which caused Verdet to come to the conclusion that the magnetic properties of the material had nothing to do with its rotary power. The "negative" rotation is now called the "paramagnetic" rotation.

A very extensive experimental examination has been made by Verdet (2) of the manner in which the constant of magnetic rotation (hence called Verdet's constant) depends on the direction of the ray with regard to the magnetic field, on the refractive power of the medium, on the dispersive power of the medium, and in the same medium on the wave-length of the light far from an absorption line. The rotation comes out, as has since been verified in detail by Du Bois, to be proportional simply to the component of the magnetic force along the ray. Media of great refractive power have in general high magnetic rotatory power. For the same medium the product of the rotatory power and the square of the wave-length is nearly constant but always increases slightly with the index of refraction; media of great dispersive power have in general also high rotatory dispersion.

Verdet's most important piece of work, however, is a precise comparison of his experimental numbers for different wave-lengths with the results of a mathematical formula adapted to express both ordinary dispersion and the magnetic rotation according to Maxwell's theory. He assumed Cauchy's form of the ordinary dispersion terms and derived the

following formula for the Verdet constant, the rotation per unit path length and unit field strength:

$$V = \frac{\theta}{LH} = m(-1/\lambda)\left[n - \lambda(dn/d\lambda)\right],$$

where $\theta$ is the rotation; m, a specific constant for the medium; H, the magnetic force resolved along the ray; L, the length of path of the ray in the medium; $\lambda$, the wave-length of the light in air; and n, the index of refraction of the medium. Comparison with experiment led to agreement within the possible errors of observation (3) for the case of carbon disulfide; but for the ordinary creosote of commerce, which is a mixture of phenols, chiefly guaiacol and creosol, the agreement was not as good. It is to be borne in mind that it is only in substances with regular dispersion (i.e., incident light far from an absorption line) that Cauchy's dispersive terms can be taken to represent the facts; whereas, the Faraday effect is related to abnormal dispersion.

Based on the assumption that the magnetic field involves rotation of the ether with velocity 1/2 k where $k = eH/m$, e being in electromagnetic units, H. Becquerel (4) derived the expression, $(1/2)(k/c)(\lambda)(dn/d\lambda)$, for the coefficient of magnetic rotation as a function of the wave-length; where c is the velocity of light in vacuum; $\lambda$, the wave-length of the light in vacuum; and n, the index of refraction of the medium. He also showed that this expression is in good agreement with actual values as regards order of magnitude and also with Verdet's detailed observations on the spectrum of carbon disulphide and creosote.

In 1884 Kundt (5) discovered that very thin films of iron gave enormous rotation when placed in a strong magnetic field, a film of

of thickness only one-third of the wave-length of light giving a rotation of the polarization plane of over 4°. An iron plate of 1 mm thickness, if it were possible to get light through it, would give under similar conditions a rotation of 66 complete revolutions while a quartz plate of equal thickness gives a rotation of only 20°. The direction of rotation was found to be positive; i.e., metallic iron behaves like the diamagnetic substances.

In his book "Lehrbuch der Optik" published in 1900 Paul Drude (6) developed two theories of magnetic rotation. The first (his own) was based on the hypothesis of molecular currents as conceived by Ampere and Weber to explain magnetism and diamagnetism. The second, due to Voigt, was based on the Hall effect. The first was later abandoned.

According to Drude's argument, a magnetic field was said to produce a greater density of the lines of force in a paramagnetic substance than in the free ether and a lesser density in a diamagnetic substance than in the free ether. Ampere and Weber had advanced the theory that so-called molecular currents existed in paramagnetic substances. According to the theory of dispersion adopted by Drude, these currents were due to the ionic charges. When an external magnetic field was applied, these molecular currents were partially or wholly turned into a definite direction so that the magnetic lines due to them were superposed upon the magnetic lines due to the external field. Thus, both in para- and diamagnetic substances in a strong magnetic field, certain ions were supposed to be in rotation and to produce molecular currents. When such an ion was struck by the electric field of a light wave, its path must be changed. The periodic electric

field of the light waves caused periodic displacements of the center of rotation or, in other words, waved the magnetic field of the molecular current to and fro. The introduction of expressions for this motion into the equation representing light propagation accounted for magnetic rotation of the plane of polarization but called for a rotation of opposite direction on opposite sides of an absorption band; in other words, an anomalous rotatory dispersion represented by a curve similar in form to the curve of anomalous dispersion shown by absorbing media. Very few cases of such a rotation have been found, and these have been explained on a different hypothesis. On this account, the hypothesis of molecular currents was abandoned.

However, there are some experimental observations in agreement with the predictions of the second theory (Voigt's). Here the assumption of rotating ions was dropped, and the concept of movable ions was taken into consideration. Every molecule of a substance consists of positively or negatively charged atoms or groups of atoms, the ions. In a conductor these ions are free to move about, but in an insulator they have certain fixed positions of equilibrium about which they may oscillate. In every element of volume the sum of the charges of the positive and negative ions must be zero. Now a strong magnetic field must exert special forces upon the ions because an ion in motion represents an electrical current, and every element of current experiences in a magnetic field a force which is perpendicular to the element and to the direction of magnetization. Consequently, the current lines in a magnetic field tend to move sideways in a direction at right angles to their direction. This phenomenon, known as the Hall effect, is

actually observed in all metals, particularly in bismuth and antimony. Thus in a magnetic field an electron which is thrown into vibration by light waves will experience a force which will be proportional to the velocity with which it is moving. By introducing an expression representing this force into the equations for wave propagation, a formula was derived by Voigt which called for rotations of very large value and similar sign on opposite edges of an absorption band.

One of the observations in support of this theory is the result of the experiments of D. Macaluso and M. Corbino (7). They showed that the vapor of sodium in a magnetic field produced large rotations of similar sign for wave-lengths immediately adjacent to the D lines. A small sodium flame placed between the poles of an electromagnet was traversed by a beam of polarized white light in the direction of the lines of magnetic force. A Nicol prism was oriented so as to extinguish completely the light when the current was not traversing the coils. On forming the magnetic field a brilliant yellow light was found to be transmitted by the Nicol. The spectroscope showed this light to consist of narrow bands symmetrically placed on each side of the D lines. By turning the Nicol first in one direction and then in the other it was easy to see that the rotation was of the same sign on opposite sides of the band. The experiment was later repeated and carried out on a large scale by R. W. Wood (8).

The first evidence that a magnetic field can affect a band spectrum of diatomic or polyatomic molecules was obtained by A. Rhigi (9) who showed that $I_2$, $Br_2$ and $NO_2$ vapors give an unusually large Faraday effect for frequencies in the region of their absorption band systems. He

inferred the existence of a Zeeman effect for these bands. The relation between the Faraday and Zeeman effect was pointed out by J. Larmor in his book "Aether and Matter" (10), published in 1900.

In 1896 P. Zeeman discovered that when the vapor of a metal, like sodium or cadmium, is brought to incandescence in a magnetic field, a narrow line in its emission spectrum is resolved into two or three lines of slightly different frequencies. The doublet is produced when the direction of the nagnetic lines is the same as the direction of emission, the triplet when these directions are at right angles to each other. Shortly afterwards, Lorentz presented a sample theory for these observations based upon the electron theory of matter. He futher predicted that in the longitudinal direction these lines should be circularly polarized and in the transverse direction, plane-polarized.

The phenomenon described in the preceding paragraph is known as the normal Zeeman effect. Later, Preston, using greater dispersion and resolving power, was able to show not only that certain lines were split up into triplets when viewed perpendicularly to the field but that others were split into as many as four, five, or even a much larger number of components. The phenomenon is called the anomalous Zeeman effect.

The Zeeman effect obtained in absorption is called the inverse Zeeman effect. The phenomenon is observed by sending white light through an absorbing vapor when the latter is subjected to a uniform magnetic field. A classical treatment of the problem shows the following results. If we let $\nu_o$ be the natural resonance frequency of the vapor in the absence of a field, then an absorption line will split into two lines, $\nu_o + \Delta\nu$ and $\nu_o - \Delta\nu$, when the magnetic field is in the direction of

the propagation of light (i.e., the longitudinal Zeeman effect). Also an absorption line will split into three lines, $\nu_o$, $\nu_o + \Delta\nu$, and $\nu_o - \Delta\nu$, when the magnetic field is perpendicular to the propagation of light. The value, $\Delta\nu$, is the angular frequency of precession of an orbit in a magnetic field and was calculated by Larmor from the classical theory to be equal to $(eH)/(4\pi mc)$, where c is the velocity of light; m, the mass of the electron in grams; e, the charge on the electron in electrostatic units; and H, the magnetic field strength in gauss.

From this theory of the Zeeman effect, Larmor gives the following deduction of Becquerel's formula for magnetic rotation: The incident plane-polarized vibration can be regarded as the resultant of two oppositely polarized circular vibrations, and these are propagated with different velocities. If $\nu$ is the frequency of the incident light through an unmagnetized medium, and if v and $v_o$ are the velocities of propagation of circular light of frequency $\nu$ in a magnetic field H and in the absence of magnetic field respectively, then

$$v = v_o \pm (dv/d\nu)\Delta\nu \text{ , where } \Delta\nu = (eH)/(4\pi mc).$$

Now if $v_1$ and $v_2$ are the velocities of the right- and left-handed components of an incident plane-polarized train of frequency $\nu$ in a magnetic field H, then

$$v_2 - v_1 = 2(dv/d\nu)\Delta\nu .$$

The rotation of the plane of polarization in length L of the medium will be $(\nu/2)(L/v_1 - L/v_2)$ cycles, the latter factor being the difference of the times of transit. Thus

$$\theta = \text{Rotation in radians} = (2\pi)(\nu/2)(L/v_1 - L/v_2)$$

$$\theta = (L\pi\nu/v^2)(v_2 - v_1) = (2\pi L\nu/v^2)(dv/d\nu)\Delta\nu .$$

If $\lambda$ is the wave-length in vacuum and n its refractive index in the medium, then $v = c/n$, $dv = -(c/n^2)dn$, $\nu = c/\lambda$, and $d\nu = -(c/\lambda^2)d\lambda$. Hence

$$\theta = (Le/2mc^2)(H\lambda)(dn/d\lambda) \text{ or}$$

$$V = \theta/LH = (e/2mc^2)(\lambda)(dn/d\lambda).$$

The above argument which applies to the normal Zeeman effect can be applied also in cases where the effect is abnormal by substituting the modified value of the Zeeman displacement.

It was established theoretically by Voigt (11) that, in the case of an absorption line separated into a magnetic doublet by the Zeeman effect, the rotation of the plane of polarization was positive for all frequencies lying outside the components of the doublet and negative for all frequencies between the components; the light traversing the medium in the direction of the lines of force. This was verified by P. Zeeman (12).

Zeeman also devised the graphical method of explaining magnetic rotation. Consider the passage of light through a vapor like sodium. There are certain resonance frequencies $\nu_o$ at each of which absorption takes place. When the magnetic field is introduced, there will be for each $\nu_o$, according to the classical theory of the Zeeman effect, two resonance frequencies, one $\nu_1$ for left circularly polarized light and the other $\nu_2$ for right circularly polarized light. For each of these directions of rotation an absorption curve and a dispersion curve may

be drawn (13). It is observed that outside the region $\nu_1$ to $\nu_2$ the value of $n^-$ is greater than $n^+$, where $n^-$ is the refractive index of the left circularly polarized light, and $n^+$ is the refractive index of the right circularly polarized light. Therefore, positive rotations travel faster than negative, and the plane of the incident polarized light is rotated in the positive direction. The difference between the two dispersion curves shows that for frequencies between $\nu_1$ and $\nu_2$ the rotation is in the negative direction.

Ladenburg and Minkowski (14) have shown that, by measuring the magnetic rotation in the vicinity of absorption lines, in cases where the density of the vapor is known, the number of resonating (or dispersion) electrons per atom, p, or the so-called "oscillator strength" of the atom for the resonance frequency in question can be calculated. The p values for the D lines of sodium calculated from magnetic rotation are 0.66 for $D_2$ and 0.33 for $D_1$, the sum being practically unity or one electron per atom (the valence electron).

It was thought for many years that the fine lines which make up band spectra were unresponsible to a magnetic field. The first observations showing an influence were made by R. W. Wood (8) during the investigation of the rotatory power of magnetized sodium vapor in 1895. With dense vapor it was observed that, with crossed Nicols, a spectrum of numerous bright lines in the red-orange and green-blue region appeared as soon as the magnetic field was turned on, showing that rotation of the plane of polarization occurred in the vicinity of the lines which made up the complicated band spectrum, which we now know results from absorption by diatomic sodium molecules. Similar results

were later obtained with iodine and other vapors. An extended study of the magnetic rotation spectrum of sodium vapor was made by R. W. Wood and F. E. Hackett (15).

From 1906 to 1909 Wood cataloged extensively lines of the magnetic rotation spectrum of $Na_2$ in the region of the red and blue-green band systems, and also measured the sign of the rotation outside six iodine absorption lines covered by the broadened mercury green line. However, he did not develop the theory for the magnetic rotation spectrum (15, 16, 17, 18).

No new observations about the magnetic rotation spectrum in band systems of molecules were made until 1928, when Loomis noticed that most of Wood's blue-green magnetic rotation lines in sodium corresponded to the heads of the absorption bands. Using magnetic rotation lines he followed the upper electronic levels very close to their convergence and was able to obtain a much improved estimate of the heat of dissociation of the molecule (19). In a series of papers, Loomis and his students have applied the method of magnetic rotation spectra to $'\pi \leftarrow {}'\Sigma$ absorption systems of other alkali molecules to determine accurately their heats of dissociation (20, 21, 22, 23, 24).

However the red magnetic rotation spectrum of $Na_2$ puzzled scientists for quite a while. Since this spectrum is due to the transition $'\Sigma - {}'\Sigma$ , it should not show any Zeeman effect nor the Faraday effect. Fredrickson and Stannard (25) succeeded in assigning quantum numbers to the magnetic rotation lines of the $Na_2$ red system which suggested strongly that perturbation of a few of the levels of the upper $'\Sigma$ state was responsible for the appearance of the magnetic rotation spectrum. Carroll (26) investigated the infrared magnetic rotation spec-

trum of $K_2$. He found that there are large groups of perturbed levels in each vibrational level, which give rise to so many magnetic rotation lines that the assignment of quantum numbers is not easy. He studied their quartz wedge spectrograms which supply the strongest evidence that $K_2$ infrared magnetic rotation spectrum is produced by perturbations just as is the red magnetic rotation spectrum of $Na_2$.

Not much data have been collected for the magnetic rotation spectra of polyatomic molecules. It has been reported that each of $NO_2$, $CS_2$, $SO_2$ and HCHO gives a magnetic rotation spectrum, but no detailed analysis has been carried out (27).

The quantum mechanical theory of the Faraday effect was first developed in 1929 from atoms by Rosenfeld (28). Rosenfeld found that, for the case of multiplet widths small compared to (kT)/h, when the frequency of the incident light is not near any absorption line, the rotation can be expressed as a sum of terms of two types: the diamagnetic, characterized by independence of temperature, and the paramagnetic, proportional to 1/T. The diamagnetic term can be written in the Becquerel form

$$V = (e/2mc^2)(\nu \frac{\partial n}{\partial \nu}).$$

This value of V is known as the normal Verdet constant.

The quantum mechanical theory of the Faraday effect in molecules was first attempted by Kronig (29) and extended by Serber (30) and Carroll (26).

Serber started with the Kramers-Heisenberg dispersion formula and applied first order perturbation theory to derive the general equation for the Faraday effect. His derivation leads to the following expression

for the Verdet constant:

$$V = \sum_{n'} \frac{\nu^2 A(n''n')}{\left[\nu(n'n'')^2 - \nu^2\right]^2} + \frac{\nu^2 B(n''n')}{\nu(n'n'')^2 - \nu^2} + \frac{\nu^2 C(n''n')}{T\left[\nu(n'n'')^2 - \nu^2\right]}$$

where $n'$, $n''$ are the quantum numbers of the upper and the ground states respectively; $\nu(n'n'')$ is the energy difference in wave numbers between the upper state and the ground state; T is the absolute temperature; $A(n''n')$, $B(n''n')$ and $C(n''n')$ are three differenct collections of terms which depend on the quantum states $n''$ and $n'$ only; and $\nu$ is the frequency of the incident light in wave numbers.

When the frequency of incident light is far from an absorption line, the first term becomes much smaller than the second and third terms and the expression is comparable to Rosenfeld's formula for atoms. However, in the immediate vicinity of an absorption line the first term is dominant and the second and third become of smaller importance. Under these circumstances Carroll showed that the first term results from the Zeeman splitting as previously interpreted on the classical theory and the second term results principally from changes in the intensity of the Zeeman components. Thus, writing $V = V_A + V_B$, $V_A$ varies symmetrically about the absorption line and is due to the Zeeman splitting, $V_B$ varies antisymmetrically and is due to intensity alterations. The $V_B$ term is calculable only by quantum mechanics and is the essential quantum mechanical refining of the theory.

# CHAPTER III

## THEORETICAL CONSIDERATIONS

The general basis of the quantum mechanical theory of the Faraday effect has been outlined in the previous chapter. In this chapter the general expression will be applied to determine under what conditions and for what transitions a Faraday effect is to be expected.

In the immediate vicinity of an absorption line the dominant term in Serber's expression for the Verdet constant is the first, i.e., that depending on the Zeeman splitting of the line. The second term, which was shown by Carroll to depend on the perturbation of the transition probabilities, is generally small compared to the first for small magnetic fields and will be neglected in this discussion. Under these conditions Serber's expression may be written explicitly as

$$V = 2CB \sum_{m''m'} \frac{\nu(n'n'')\ \nu^{(1)}(n'm';n''m'')\left[P_x(n''m'';n'm')P_y(n'm';n''m'')\right]e^{-\frac{W_{n''}}{kT}}}{\left[\nu^2 - \nu(n'n'')^2\right]^2} \qquad (1)$$

where $B = N/\sum_{n''} e^{-\frac{W_{n''}}{kT}}$ ; $C = (4\pi^2\nu^2 i)/ch$; $i = \sqrt{-1}$; $n''$ and $n'$ represent the quantum numbers of the ground and upper states; $m''$ and $m'$ are the quantum numbers which differentiate the various states within an electronic state; $\nu(n'n'')$ is the energy difference in wave numbers between the upper state and the ground state; $\nu$ is the frequency of the incident light in wave numbers; $\nu^{(1)}(n'm';n''m'')$ is the difference in wave numbers between the lines into which an absorption line is split in a magnetic field; $W_{n''}$ is the internal energy of the ground state $n''$;

xyz is a set of coordinates which is fixed in space; $P_x(n''m'';n'm')$ is the matrix element of the x-component of the dipole moment between the states $(n''m'')$ and $(n'm')$; and the square bracket $[P_x(n''m'';n'm')P_y(n'm';n''m'')]$ stands for the difference between $P_x(n''m'';n'm')P_y(n'm';n''m'')$ and $P_y(n''m'';n'm')P_x(n'm';n''m'')$. The magnitude of the factors in the expression (1), and hence the dependence of V on the rotational quantum number J, depend strongly on the nature of the electronic transition.

The electronic states of diatomic molecules are best characterized according to the manner in which the different angular momenta in the molecule-electron spin, electronic orbital angular momentum, angular momentum of nuclear rotation - are coupled together to give the total angular momentum J. In general, we can classify all diatomic molecules approximately into five extreme coupling cases which are called Hund's case (a), (b), (c), (d) and (e). Only the first three coupling cases are of practical importance. The magnetic rotation spectra of molecules for these three cases will be discussed in detail, and formulas for the Verdet constant for each of these three cases will be derived.

Case (a) coupling is typified by the alkali molecules $Na_2$, $K_2$, $Li_2$, NaK, and $Rb_2$. In case (a), the electronic states are characterized by quantum numbers S, $\Lambda$, $\Sigma$ and $\Omega$, where S is the total spin angular momentum, $\Lambda$ is the component of the electronic orbital angular momentum along the internuclear axis, $\Sigma$ is the component of the total spin angular momentum along the internuclear axis, and $\Omega$ is the quantum number of the resultant electronic angular momentum about the internuclear axis. For such molecules the Zeeman splitting of the excited state is given by the simple expression (31).

$$W^{(1)} = \bar{\mu}_H(n',m') \tag{2}$$

with $$\bar{\mu}_H(n',m') = \frac{(\Lambda + 2\Sigma)(\Lambda + \Sigma)M}{J(J+1)} \mu_o \tag{3}$$

where H = the strength of the magnetic field;

$\bar{\mu}_H(n',m')$ = the mean value of the component of the magnetic moment in the field direction;

$\mu_o$ = a Bohr magneton;

J = quantum number of the total angular momentum (rotational quantum number) of the molecule. Superscript " means the ground state, and superscript ' indicates the upper state of the particular transition;

M = the component of the total angular momentum J in the direction of the magnetic field.

$W^{(1)}$ is defined by the relation $W = W_o - W^{(1)}_H$;

W = the energy of the molecule in a magnetic field; and

$W_o$ = the energy of the molecule in the absence of a magnetic field.

If the ground state of the transition has no Zeeman splitting, which will be the case for almost all stable molecules, then we have

$$\nu^{(1)}(n',m';n''m'') = W^{(1)}(n'm'). \tag{4}$$

The elements of the x and y components of the electric moment for a symmetric top molecule have been calculated by Kronig (29) as follows:

$$P_x(J,M:J-1,M\mp1)P_y(J-1,M\mp1;J,M) = \mp \frac{iP^2(J-1)(J\pm M)(J\pm M-1)}{2J(2J-1)(2J+1)};$$

$$P_x(J,M;J+1,M\mp1)P_y(J+1,M\mp1;J,M) = \pm \frac{iP^2(J+2)(J\mp M+2)(J\mp M+1)}{2(J+1)(2J+1)(2J+3)}; \qquad (5)$$

$$P_x(J,M;J,M\mp1)P_y(J,M\mp1;J,M) = \pm \frac{iP^2(J\mp M+1)(J\pm M)}{2J(J+1)};$$

where $P = P_{x'}(n'n'')$ and is the electronic transition moment for a set of coordinates x', y', z' which are rotating with the molecule such that the z' axis lies along the internuclear axis.

Substituting equations (2, (3), (4) and (5) into equation (1), the Verdet constant becomes

$$V = \frac{4\pi e \nu_1 P^2 \nu^2 B(e^{-\frac{W_J''}{kT}})f(J'')}{3hmc^2(\nu^2 - \nu_1^2)^2}, \qquad (6)$$

where $f(J'') = (J'' + 2)/(J'' + 1)$ for R branch;

$f(J'') = -(J'' - 1)/J''$ for P branch;

$f(J'') = (2J'' + 1)/J''(J'' + 1)$ for Q branch; and

$\nu_1 = \nu\,('\pi,'\Sigma)$.

This result was obtained by Serber (30) for the particular transition $'\pi-'\Sigma$ of the alkalis.

Case (b) and case (c) couplings differ from case (a) primarily in the expression for $\nu^{(1)}(n'm';n''m'')$. The Zeeman splitting for case (c) is derived in the appendix and leads to the following results:

$$\Delta_H = (KM\Omega^2\mu_0)/J(J + 1); \qquad (7)$$

where

$$K = \frac{-L(L+1)+S(S+1)+3J_a(J_a+1)}{2J_a(J_a+1)} \quad .$$

Hence for transitions from $^1\Sigma$ ground states,

$$\nu^{(1)}(\Omega J'M';0J''M'') = (KM'\Omega^2\mu_0)/hJ'(J'+1),$$

and

$$V = \frac{4\pi e\, \nu_1 P^2 \nu^2 BK\Omega^2 (e^{-\frac{W_{J''}}{kT}}) f(J'')}{3hmc^2(\nu^2 - \nu_1^2)^2} , \qquad (8)$$

where $f(J'') = (J'' + 2)/(J'' + 1)$ for R branch;

$f(J'') = -(J'' - 1)/J''$ for P branch;

$f(J'') = (2J + 1)/J''(J'' + 1)$ for Q branch; and

$\nu_1 = \nu_1(X,{}^1\Sigma)$, X denotes an upper state which has the resultant electronic angular momentum $\Omega$ about the internuclear axis.

For case (b) coupling, the Zeeman splitting is given by Herzberg (32) as follows:

$$\bar{\mu}_H = \left[\frac{\Lambda^2}{\sqrt{K(K+1)}} \cos(K,J) + 2\sqrt{S(S+1)}\cos(S,J)\right] \frac{M}{\sqrt{J(J+1)}} \mu_0 \qquad (9)$$

where $K = \Lambda, \Lambda+1, \Lambda+2, \Lambda+3, \ldots\ldots$

$J = (K+S), (K+S-1), \ldots\ldots\ldots\ldots; \quad K-S$

$M = \pm J.$

This value $\bar{\mu}_H$ may be used as in Hund's case (c) coupling to derive the expression for the Verdet constant. However in case (b) coupling, it very often happens that the coupling between S and K is so weak that

these two angular momenta are uncoupled even by a small field. The molecular analogue to the Paschen-Back effect then appears. S and K are space quantized independently of each other in the field direction with components $M_S$ and $M_K$. As a result $\bar{\mu}_H$ is given by the simpler formula:

$$\bar{\mu}_H = \frac{\Lambda^2 M_K}{K(K+1)} \mu_o + 2M_S \mu_o. \qquad (10)$$

Hence

$$W^{(1)} = \frac{\Lambda^2 M_K}{K(K+1)} \mu_o + 2M_S \mu_o.$$

For $^2\Pi - {}^2\Sigma$ transitions,

$$\nu^{(1)}(1K'M_K';0K''M_K'') = \frac{M_K'}{h\, K'(K'+1)} \mu_o$$

The term involving $M_S$ does not appear here, because when the Paschen-Back effect is present in both states participating in a transition, the selection rules ($\Delta M_S = 0$) holds. Substituting the value of $\nu^{(1)}$ and the values for the elements of the electric moment into equation (2), we get the Verdet constant, V:

$$V = \frac{4\pi e \nu_1 P^2 \nu^2 B \left(e^{-\frac{W_K''}{kT}}\right) f(K'')}{3hmc^2(\nu^2 - \nu_1^2)^2}$$

where $f(K'') = (K''+2)/K''+1)$ for R branch;

$f(K'') = -(K''-1)/K''$ for P branch;

$f(K'') = (2K''+1)/K''(K''+1)$ for Q branch; and

$\nu_1 = \nu(^2\Pi, {}^2\Sigma)$.

Hence we will expect the magnetic rotation spectrum for the transition $^2\Pi - ^2\Sigma$ to consist of lines which correspond to the band origins of the absorption spectrum. It may be worthwhile to investigate this problem for BO, CN and the hydrides of the alkaline earth metals. However, these are not included in the present investigation.

In the preceding paragraphs, the Verdet constants in diatomic molecules for Hund's cases (a), (b) and (c) couplings have been derived. Some transitions have been found which should not give any magnetic rotation spectrum according to formulas (6), (8) and (11), but for which magnetic rotation spectra have been found by experiment. It will be shown later that this does not indicate any violation of the theory just discussed, but some other factors like rotational distortion and pertubations have entered the picture.

According to formula (8) for Hund's case (c) coupling, the transition $^3\Pi_o - {}^1\Sigma$ should not give any magnetic rotation spectrum. But it has been known since 1898 that $I_2$ and $Br_2$ both give magnetic rotation spectra in the green region. The reason for the magnetic rotation spectrum of $Br_2$ has not been given in the literature and will be discussed later in Chapter V. $I_2$ gives a magnetic rotation spectrum because of rotational distortion, that is, the effect of molecular rotation in uncoupling the spin from the internuclear axis. Serber (30) succeeded in deriving a formula for the Verdet constant, V, in the case of rotational distortion:

$$V = \mp \frac{16\pi e b \nu_1 P^2 \nu^2 B(e^{-\frac{W_{J'\pm1}}{KT}}) J'(J+1)}{3hmc^2 \nu_2 (\nu^2 - \nu_1^2)^2}, \qquad (12)$$

where the minus sign is to be taken for the R branch and the plus for the P branch; J' is the total angular momentum (or the rotational

quantum number) of the upper state, $^3\Pi_o$; $\nu_1 = \nu(^3\Pi_o, {}^1\Sigma)$ and $\nu_2 = \nu(^3\Pi_o, {}^3\Pi_1)$. From the nature of rotational distortion, we should expect that the faster the rotation, the larger the magnetic moment that will be produced. This explains why the magnetic rotation lines in $I_2$ appear to correspond to absorption lines of high J and to be weak or absent near band origins. Formula (12) shows this result.

In Hund's case (a) coupling, the transition $^1\Sigma - {}^1\Sigma$ should give V = 0 and thus no magnetic rotation spectrum. But this transition in the molecules $Na_2$ and $K_2$ does give an infrared magnetic rotation spectra. Fredrickson and Stannard (25) succeeded in finding an assignment of quantum numbers for the lines of the red $Na_2$ magnetic rotation spectrum. They discovered that most of the lines involved a certain few of the rotation levels in the upper state and suggested on this basis that the spectrum is due to a perturbation of the upper state by a $^3\Pi$ state. Carroll (26) found that, in $K_2$, there are large groups of perturbed rotational levels in each vibrational level, which give rise to so many magnetic rotation lines that he was unable to assign quantum numbers to the perturbed levels. During the present investigation, IBr was discovered to give a magnetic rotation spectrum for the $^3\Pi_o - {}^1\Sigma$ transition, which should not appear according to formula (7). It is believed that the magnetic rotation spectrum found is due to a perturbation.

For polyatomic molecules the lines of absorption spectra lie so closely together that there is not much hope of detecting any splitting due to the Zeeman effect. This may be the reason why there is hardly any discussion of the Zeeman effect for polyatomic molecules

in the literature. However, some polyatomic molecules do have small magnetic moments in their molecular levels. One of the best ways to study these molecular levels is through the study of their magnetic rotation spectra. It has been reported that $NO_2$ and $CS_2$ give strong magnetic rotation spectra, and $SO_2$ and HCHO give weak ones in the ultraviolet region. It seems possible that the weak magnetic rotation spectrum of $SO_2$ is due to a singlet-triplet transition. In $NO_2$ the transitions involved are $^2A_1 - {}^2A_1$ and $^2B_1 - {}^2A_1$ which may be approximated as $^2\Sigma - {}^2\Sigma$ in Hund's case (b) coupling of diatomic molecules (33). According to formula (10), $^2\Sigma - {}^2\Sigma$ transition will have V = 0 and thus will not give any magnetic rotation spectrum. But if the doublet splitting without the field is appreciably greater than the normal Zeeman splitting, formula (9) should be used instead of (10). Thus we have

$$\bar{\mu}_H = \frac{2\sqrt{S(S+1)}\cos(S,J)\, M\mu_o}{\sqrt{J(J+1)}} . \qquad (13)$$

Referring to Figure 144 in Herzberg's Spectra of Diatomic Molecules (31), it can be easily shown by the law of cosines that

$$\cos(S,J) = \frac{S(S+1) + J(J+1) - K(K+1)}{2\sqrt{S(S+1)\, J(J+1)}} .$$

Thus

$$\bar{\mu}_H = \left(\frac{S(S+1) - K(K+1)}{J(J+1)} + 1\right) M\mu_o , \text{ and}$$

$$\nu^{(1)} = (M'-M'')\mu_o + \left(\frac{S'(S'+1)-K'(K'+1)}{J'(J'+1)}M' - \frac{S''(S''+1)-K''(K''+1)}{J''(J''+1)}M''\right)\mu_o$$

For $S \neq 0$, the Verdet constant, V, will be different from zero. Hence $NO_2$ may have complex magnetic rotation spectra.

As we have noticed, there are different reasons such as the Zeeman splittings, rotational distortion, and perturbations which are responsible for the appearance of magnetic rotation spectra of molecules. For diatomic molecules we can differentiate between them in most cases. The magnetic rotation spectrum due to the Zeeman effect in the upper state, like in the transitions $^3\Pi_1 - {}^1\Sigma$ of ICl and $^1\Pi - {}^1\Sigma$ of $Na_2$, usually consists of lines which correspond to the band origins of the absorption spectrum. Rotational distortion gives lines of high J values only, while perturbations produce lines, most of which involve a certain few rotational levels in the upper state. These arguments for diatomic molecules can be extended to linear polyatomic molecules, since both behave as symmetric tops. An example is the intense magnetic rotation spectrum of linear $CS_2$ in the region between 3640A and 3355A (34). It consists of doublets with 17 $cm^{-1}$ separation, and there is an excellent correlation between the sharp absorption edges and the low frequency member of the magnetic rotation doublets. It has been concluded that the molecule has a magnetic moment along the figure axis in the upper state of the transition. For non-linear molecules, the theory for magnetic rotation spectra is still in the state of development.

The above results can be summarized here. Strong magnetic rotation spectra are expected for transitions in which a change in magnetic moment along J is expected. Thus, transitions of the type $^1\Pi - {}^1\Sigma$, $^3\Pi_1 - {}^1\Sigma$, $^3\Sigma - {}^1\Sigma$, $^2\Sigma - {}^2\Sigma$ (weak field), etc. are expected.

No strong transitions are expected for $^1\Sigma - {}^1\Sigma$, $^3\Pi_0 - {}^1\Sigma$, $^2\Sigma - {}^2\Sigma$ (strong field), etc. Weak transitions occur in violation of these predictions if rotational distortion or other perturbations cause mixing of non-magnetic levels with nearby magnetic levels. It must be noted that a sharp line spectrum is required for the presence of any magnetic rotation spectrum since the Zeeman splitting must be appreciable compared to the line width.

# CHAPTER IV

## INSTRUMENTS AND PROCEDURES

Apparatus was set up as shown in Figure 1. It consisted of a light source, a collimating lens, a defining aperture, a polarizer, an optical cell inside a longitudinal electromagnet, a second aperture, an analyzer, a system of lenses and a spectrograph. A side arm on the optical cell was provided for evacuating the cell and for introducing gaseous samples.

A Western Union Concentrated-Arc Lamp (manufactured by the Western Union Telegraph Co., Water Mill, New York) was used as a light source because it has a source diameter of 1.50 mm which is close enough to a point source to satisfy the requirements of the polarizers used in this investigation. This lamp operates in argon at atmospheric pressure by ionic bombardment of a metallic film of metallic zirconium or zirconium oxide. It is a DC lamp operated from a suitable rectifier that provides high voltage for starting and low voltage for operation. Under operating conditions, it consumes 100 watts at a voltage of 15.4 volts. It has maximum brightness of 5200 candles per $cm^2$, average brightness of 3900 candles per $cm^2$, candle power of 77 and an average life of 1000 hours. The cathode of this arc lamp consists of a cup of tungsten, molybdenum, or tantalum packed with zirconium oxide; the anode is a sheet or plate of similar metal. The spectrum exhibits a continuum from the incandescent zirconium metal (temperature about 3000°K), superimposed upon which are argon and zirconium lines from

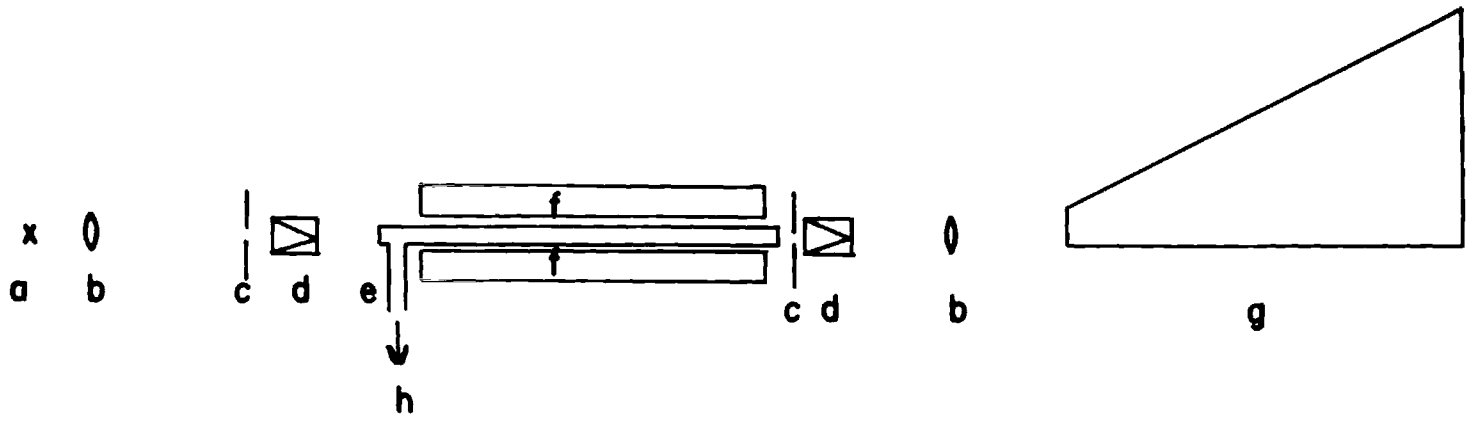


Figure 1

Apparatus for the Study of Magnetic Rotation Spectra of Molecules

(a) Light Source; (b) Collimating Lens; (c) Defining Aperture; (d) Ahrens Prism; (e) Optical Cell; (f) Electromagnet; (g) Spectrograph; (h) Sample Compartment.

the arc stream. Besides this lamp, an iron arc on a CENCO (Central Scientific Company) arc support could be introduced into the optical system by inserting a mirror after the analyzer without disturbing any part of the optical system. This iron arc spectrum was photographed on each film for the calibration of wave-lengths.

The collimating lens for the light source was a simple double convex lens with focal length of 12.5 cm. The light source was placed at the focal point of the lens, so that the light would emerge through the lens in a parallel beam. The lens system in front of the spectrograph with a combination of an achromatic lens with a cylindrical lens. They were so adjusted that the light was focused on the slit of the spectrograph as a narrow vertical line. Both the polarizer and the analyzer were the Ahrens prisms of 12 mm aperture.

The optical cell was made of pyrex tubing. It was 49.5 cm long and had an inside diameter of 1.3 cm. The two ends of the tubing were carefully ground and polished and windows of polished pyrex plate glass were sealed onto it with "Apiezon W" wax. The optical cell had a side arm which was connected through a stopcock to a vaporization compartment. The other side of the vaporization compartment was connected through a stopcock and a soda-lime tube to a mercury manometer and a vacuum pump. The vaporization compartment was essentially a T-tube with a standard taper ground-glass joint, onto which a tube with a mating joint can be attached. The optical cell had a cooling jacket consisting of a pyrex tube of inside diameter 2.9 cm. For several experiments, a thermocouple with copper-constantan thermo-elements was attached onto the outer wall of the cooling jacket, and was insulated

from the inner walls of the electromagnet with three layers of asbestos paper. The thermocouple was used to measure the temperature of the gaseous sample inside the optical cell by means of a potentiometer. For other experiments, a mercury thermometer was inserted in the cooling jacket for the same purpose.

The electromagnet was constructed by winding copper wire (No. 14) around a copper tube 1.5 inches in diameter. It had an inner jacket for water cooling. Two steel bars were used as pole pieces and also as a support for the magnet since the central copper tube rested on these two steel bars. In order to complete the circuit for magnetic flux, a large piece of steel plate was bolted to the two bars. This electromagnet had a field strength of about 1000 gausses when a direct current of 4.8 amperes was sent through it, and of about 1250 gausses with a current of 5.6 amperes.

For the study of absorption and magnetic rotation spectra, the three-meter replica grating spectrograph (J. A. 78) of Jarrell Ash Company was employed. It has a four-inch replica concave grating with 15,000 lines per inch, mounted in the Wadsworth stigmatic arrangement. The spectrograph has first order dispersion of 10.9 A/mm and a resolution believed to be better than 0.2A. Films were developed in the ARL (Applied Research Laboratory) developing machine and dried with the infrared lamp on the ARL film dryer.

Gaseous samples were introduced in the following way. A tube with the condensed liquid or solid sample in a dry-ice methanol bath was introduced in the vaporization compartment. The entire system was evacuated to a high vacuum. Then the pump and the soda-lime tube were

cut off with a stopcock. The dry-ice bath was removed and the sample was allowed to warm up to a temperature which would give the desired vapor pressure. The stopcock to the optical cell was then closed and the system was ready for the study of the magnetic rotation spectrum.

Photographic device was used. After the camera on the spectrograph was loaded with film (Kodak film type 103-F for the visible region and type 1 N for the infrared region); the light source excited; polarizer and analyzer set to extinction; and the electromagnet activated with direct current, the magnetic rotation spectrum was then photographed on the film through the spectrograph. Absorption spectra were taken with polarizer and analyzer set in such position that their optical axes were parallel to each other. An iron arc spectrum was always introduced onto each film above and below the rotation spectrum for the calibration of wave-lengths. Exposure for the magnetic rotation spectra in the visible region ranged from two to ten hours with a slit width of 100 microns.

Exposed films were developed with D-19 developer (3 minutes for film type 103-F and 7 minutes for film type 1 N at 68° F), fixed with Kodak rapid liquid fixer, washed, and dried with the infrared lamp. Spectral lines on the film were traced automatically by means of a recording microphotometer, which has been described in detail by F. S. Wilson (35). Since all the iron arc lines in this region had been known to high accuracy, the wave-lengths of magnetic rotation lines and absorption lines could be measured and converted to wave numbers by using Kayser's Table (36).

The main interest of this investigation is the study of magnetic

rotation spectra of $I_2$, ICl, IBr (with natural bromine), natural $Br_2$ $Br^{79}Br^{79}$, $Br^{81}Br^{81}$, $IBr^{79}$ and $IBr^{81}$. However, the compound $NO_2$ was also studied as an introductory step for the study of other polyatomic compounds. $I_2$ and natural $Br_2$ were commercially available. ICl was prepared by mixing about 0.2 moles of solid iodine with 0.3 moles of liquid chlorine in a tube which was kept in a dry-ice methanol bath. ICl was formed when the tube was allowed to warm up slowly to room temperature. The tube was reimmersed into the dry-ice bath, and the excess chlorine was pumped off (37). IBr was prepared in a similar way.

$Br^{79}Br^{79}$, $Br^{81}Br^{81}$, $IBr^{79}$ and $IBr^{81}$ were prepared from $AgBr^{79}$ and $AgBr^{81}$, which were obtained on loan from the Atomic Energy Commission through the Oak Ridge National Laboratory. Since these isotopic bromines had to be returned, a very careful study was made for the quantitative conversion of AgBr into $Br_2$. Several procedures were tried. Heating AgBr above 700°C (about 900°C) with induction heating vaporized AgBr with little decomposition. When AgBr and $K_2Cr_2O_7$ were heated together at about 600°C, some bromine was produced but the temperature was too high for pyrex tubes. When AgBr, $AgNO_3$ and $K_2Cr_2O_7$ were heated at 200°C, some $NO_2$ came over. A mixture of $AgNO_3$ (76% by weight) and AgBr (24% by weight) melted at about 155°C, and gave off gases at 200°C. These gases were colorless and hence they were not bromine. When AgBr, $K_2Cr_2O_7$ and concentrated $H_2SO_4$ were heated, bromine was evolved. This method was further tested quantitatively, and 96% of the theoretical yield of $Br_2$ was obtained.

The final procedure adopted here is described below and was applied to both $AgBr^{79}$ and $AgBr^{81}$. A special apparatus was designed

and constructed for the preparation of bromine from silver bromide. It consisted simply of a reaction tube and a condensing tube attached to a vacuum manifold with standard-taper ground-glass joints. These tubes could easily be removed from or inserted onto the apparatus when the system was at atmospheric pressure. All the ground glass joints were lubricated with Dow-Corning Silicone grease. About 0.12 g silver bromide, 0.7 g potassium dichromate and 10 ml concentrated sulfuric acid were mixed in the reaction tube, which was then kept at room temperature for two hours with a slight vacuum in the system. Then the tube was immersed in a bath of boiling water for two hours. At all times the condensing tube was kept in a liquid nitrogen bath. After the completion of the oxidation from silver bromide to bromine, the last trace of bromine from the sulfuric acid solution was removed by continuous pumping for fifteen minutes. This condensing tube with isotopically enriched bromine was inserted onto the vaporization compartment of the apparatus for the study of its absorption and magnetic rotation spectra.

Iodine monobromide with the isotopically enriched bromine was prepared by vaporizing iodine at 30°C into the evacuated optical cell of Figure 1. Then equal moles of isotopically enriched bromine were introduced into the optical cell by keeping the tube with bromine at -20°C and controlling the amount introduced by means of the stopcock. The completion of the reaction could be followed by the disappearance of the iodine absorption spectrum which is very intense and easily distinguishable.

The excess isotopically enriched bromine was converted into ammonium bromide with ammonium hydroxide. About 3 ml of prechilled methyl

alcohol was added to the tube containing bromine cooled in a dry-ice bath. This methanol served the purpose of slowing the reaction between bromine and ammonium hydroxide. Then 5 ml of 1 N ammonium hydroxide were added slowly. The tube was lifted out of the dry-ice bath, and allowed to warm up to room temperature slowly. In the course of time, both bromine and ammonium hydroxide would diffuse into methanol and react there to form ammonium bromide with evolution of nitrogen. The ammonium hydroxide solution of ammonium bromide was dried in an oven thermostated at 70°C.

Iodine monobromide was converted into ammonium bromide in the following way. First it was treated in a manner similar to that used for the conversion of AgBr to bromine. 5 cc of dichromate solution which was made by dissolving 8.15 g of $K_2Cr_2O_7$ in 100 cc of concentrated sulfuric acid was added. This bromine was liberated as in the procedure described above for AgBr and condensed in a tube submerged in a dry-ice bath. It was converted into ammonium bromide with methyl alcohol and ammonium hydroxide as described in the previous paragraph. Since there was the possibility that some iodine might come over with bromine from iodine monobromide, the ammonium bromide obtained might contain a trace of ammonium iodide. In order to removed the impurity in the bromide, excess silver nitrate was added to the solution containing ammonium bromide after the solution was acidified with dilute nitric acid. The precipitated silver halide was dried, and treated with 5 cc of the dichromate solution to liberate the bromine. This time iodine was in the form of iodate and the bromine came over without any contamination. Bromine was converted into ammonium bromide was before.

# CHAPTER V

## RESULTS AND DISCUSSION

The visible absorption spectra of the diatomic halogen molecules (except $F_2$) and interhalogen compounds are known and have been partially analyzed. For $I_2$ and $Br_2$, the main band systems have been shown to be due to transitions between an excited $^3\Pi_{0^+}$ state and the ground state $^1\Sigma$. Weak band systems believed to be due to an excited $^3\Pi_1$ state are also known. For ICl and IBr, we also have systems of $^3\Pi_{0^+} \leftarrow {}^1\Sigma$ and $^3\Pi_1 \leftarrow {}^1\Sigma$ transitions. However, the $^3\Pi_{0^+}$ states of ICl and IBr are predissociated. The potential curve of a repulsive $0^+$ state, derived from normal atoms, crosses that of the $^3\Pi_{0^+}$ state. The interaction between the two $0^+$ states is such as to produce, in effect, two new but not independent states, which will still be denoted as $^3\Pi_{0^+}$ and $0^+$ states (38).

For all the halogen atoms, the ground state is $^2P$ with the $^2P_{3/2}$ component the lower and the $^2P_{1/2}$ component the higher; the separations for Cl, Br, and I are 881, 3685 and 7598 $cm^{-1}$ respectively. There are no other low-lying atomic states to interest us. The $^3\Pi_1$ states of all the diatomic halogen molecules and interhalogen compounds dissociate into normal atoms ($^2P_{3/2}$)(39). The $^3\Pi_{0^+}$ states dissociate into one normal and one excited atom. Thus one would expect one normal I atom and one excited Cl atom from ICl, and one normal I atom and one excited Br atom from IBr. However, the predissociation of $^3\Pi_{0^+}$ state with the repulsive $0^+$ state in ICl and IBr may allow the resulting $^3\Pi_{0^+}$

state to pass over a potential energy hump and to predissociate into two normal atoms. The resulting $0^+$ state produces one normal iodine atom and one excited Cl or Br atom (40,41).

A search for the magnetic rotation spectra of diatomic halogen molecules and interhalogen compounds such as ICl, IBr, $Br_2$ and $I_2$ has been made. The spectral regions investigated ranged from the near infrared to the near ultraviolet. The results on individual molecules are described and discussed below.

Iodine Monochloride.--Iodine monochloride gives a strong magnetic rotation spectrum from 6682A to 5779A in the 49.5 cm cell at a vapor pressure of 29 mm and at a temperature of 29°C. Raising the temperature increases the population in the second and third vibrational levels of the ground electronic state, and thus shifts the whole spectrum to longer wave lengths. The magnetic rotation spectrum of 29°C consists of more than a hundred bright lines. Forty-four lines could be identified with the band origins in the known absorption spectrum of $ICl^{35}$ (42), and are listed in Table 1. Eighteen lines could be identified with the band origins in the absorption spectrum of $ICl^{37}$, and are listed in Table 2. The rest of the lines are concentrated in the region between 5779A and 6000A, and could not be correlated with the band origins of the absorption spectrum. The most intense lines of this set are listed in Table 4; others were observed but appeared exceptionally weak and perhaps spurious and have been omitted from this Table. In Table 1, it should be noticed that the intensity of the lines dropped suddenly at 5813.8 A; the lines at shorter wave lengths are much weaker than those at longer wave lengths.

Based on the theories which have been developed in Chapter III, "Theoretical Considerations," most of the magnetic rotation lines of ICl may be explained. Since these lines appear in the spectral region for the $^3\Pi_1 \leftarrow {}^1\Sigma^+$ transition of ICl and since ICl follows Hund's case (c) coupling, formula (8) may be applied. It shows that the Verdet constant, V, is proportional to the factor

$$\left(e^{-\frac{W_{J''}}{kT}}\right) f(J'')$$

where $W_{J''} = B''J''(J''+1)$. The expressions for $f(J'')$ are given explicitly for the P, Q, and R branches in Chapter III and from these expressions it can be seen immediately that for the P and R branches, $f(J'')$ is independent of J" for large J" values, and that for the Q branch, $f(J'')$ diminishes as $1/J''$. Thus the Verdet constant falls off rapidly as J" increases, and has a maximum value when J" equals zero. Thus all the rotational lines for low J" values should give magnetic rotation lines. However, since the spectrograph used does not have the resolution required to separate these individual rotational lines, an entire vibrational band will appear as one bright line with its center of gravity near the band origin. Hence the magnetic rotation spectrum should consist of bright lines which correspond to the band origins of the absorption spectrum. This explains the lines listed in Table 1.

The iodine monochloride prepared from natural chlorine actually consists of two species of $ICl^{35}$ and $ICl^{37}$. $ICl^{35}$ is three times as abundant as $ICl^{37}$ and consequently lines ascribed to $ICl^{35}$ are approximately three times as intense as those ascribed to $ICl^{37}$. For this reason the band origins (usually only the band heads are measured)

in the absorption spectrum of $ICl^{35}$ are generally tabulated, and those of $ICl^{37}$ are reported in the form of the isotopic shifts, $\delta\nu$, where $\delta\nu = \nu(ICl^{35}) - \nu(ICl^{37})$. Among the magnetic rotation lines of ICl, eighteen lines could be assigned to the $ICl^{37}$, and are listed in Table 2. These lines should also correspond closely to the band origins which can be estimated for the absorption spectrum of $ICl^{37}$ by means of the formula (43)

$$\nu = 13558.0 + 205.263(v'+1/2) - 1.86488(v'+1/2)^2 - 0.0315446(v'+1/2)^3$$

for $v'' = 0$ (see the note appended to Table 2). From these $\nu$ values, $\delta\nu$ could be calculated and are listed in Table 2 and plotted in Figure 5. It is apparent that our observed values agree quite well with the values calculated in this way. The isotopic shifts in the absorption spectrum of ICl have been studied by Gibson (44) and Patkowski and Curtis (45). Their reported values do not agree with the calculated ones as well as our data from magnetic rotation lines.

The sudden drop in intensity of the lines listed in Tables 1 and 2 after $v' = 28$ for both isotopic species may indicate that the upper electronic state, $^3\Pi_1$, is perturbed by another state, and thus predissociates near 5813.8A. This suggestion is also substantiated by the anomalous magnitude of the $\Delta G'$ value between $v' = 28$ and $v' = 29$ and the deviation from linearity of the $\Delta G'$ vs $v'$ curve in this region. It should be noted that although the anomalies in $\Delta G'$ are evidenced in the absorption spectrum, no anomalous drop in intensity after $v' = 28$ is indicated.

From the theoretical consideration of Mulliken (39) the only

possible perturbing states are $0^-$ ($^3\Pi$), 1 ($^1\Pi$), $0^+$ ($^1\Sigma^+$) and $0^-$ ($^1\Sigma^-$). If $^1\Pi$ is involved and the perturbation is spin orbit, we should get strong magnetic rotation lines near the cross-over region. As the rapid falling off in intensity at $v' = 28$ was observed, it does not seem likely that $^1\Pi$ is the perturbing state. This argument favors $0^+$ ($^1\Sigma^+$), $0^-$ ($^1\Sigma^-$), or $0^-$ ($^3\Pi$) as the perturbing state. The last mentioned state seems to be the most probable one, since $0^-$ ($^3\Pi$) could acquire magnetic properties through rotational distortion and give magnetic rotation lines for large J" values. This suggestion may explain the unassigned and complicated set of magnetic rotation lines of ICl in Table 4.

Iodine Monobromide.--Iodine monobromide gives a magnetic rotation spectrum which does not have any similarity with that of iodine monochloride. The spectrum appears between 5517A and 5701A, and consists of three separate bands of a distance of about 266 $cm^{-1}$ between neighboring bands. Each band has many fine lines, among which two lines have the highest intensity and are at about 30 $cm^{-1}$ from each other (Table 4).

The spectrum occurs in the spectral region which has been identified with the $0^+ \leftarrow {}^1\Sigma^+$ transition in the absorption spectrum (41). The upper state $0^+$ is non-magnetic and should not give any magnetic rotation spectrum. However, if it is perturbed by a magnetically active state at certain points with the fulfillment of the required selection rules for perturbation, the transitions from the first, second and third vibrational levels of the ground state to these points will constitute the three separate bands as observed. Since $W_e'' = 268.4$ $cm^{-1}$ and $W_e''X_e'' = 0.78$ $cm^{-1}$ for $IBr^{79}$, the neighboring bands will be at a distance of about 266 $cm^{-1}$ from each other. From the predicted electronic

Table 1. Magnetic Rotation Lines of $ICl^{35}$ with Corresponding Band Heads of its Absorption Spectrum

| Wave-length in A. | Frequency in $cm^{-1}$ | Intensity* | Vibrational Assignment v'' | v' | Absorption Band Heads** in $cm^{-1}$ |
|---|---|---|---|---|---|
| 5782.6 A | 17288.5 $cm^{-1}$ | 2 | 0 | 32 | 17300.1 $cm^{-1}$ |
| 5787.3 | 17274.4 | 2 | 0 | 31 | 17281.0 |
| 5794.6 | 17252.7 | 2 | 0 | 30 | 17257.7 |
| 5802.2 | 17230.1 | 2 | 0 | 29 | 17232.7 |
| 5813.8 | 17195.7 | 8 | 0 | 28 | 17201.3 |
| 5824.8 | 17163.2 | 8 | 0 | 27 | 17166.5 |
| 5838.1 | 17124.1 | 8 | 0 | 26 | 17125.9 |
| 5853.4 | 17079.4 | 9 | 0 | 25 | 17080.4 |
| 5871.0 | 17028.2 | 9 | 0 | 24 | 17028.7 |
| 5891.8 | 16968.1 | 9 | 0 | 23 | 16970.2 |
| 5915.0 | 16901.5 | 10 | 0 | 22 | 16901.2 |
| 5941.8 | 16825.3 | 10 | 0 | 21 | 16826.9 |
| 5971.2 | 16742.4 | 10 | 0 | 20 | 16744.0 |
| 6003.6 | 16652.1 | 10 | 0 | 19 | 16653.8 |
| 6039.7 | 16552.5 | 10 | 0 | 18 | 16555.3 |
| 6078.5 | 16446.9 | 9 | 0 | 17 | 16447.9 |
| 6120.9 | 16333.0 | 8 | 0 | 16 | 16333.7 |
| 6166.9 | 16211.1 | 7 | 0 | 15 | 16212.6 |
| 6216.2 | 16082.6 | 6 | 0 | 14 | 16084.1 |
| 6269.0 | 15947.1 | 4 | 0 | 13 | 15947.6 |
| 6325.1 | 15805.7 | 3 | 0 | 12 | 15806.1 |
| 6385.3 | 15656.6 | 2 | 0 | 11 | 15657.3 |
| 6448.6 | 15503.0 | 2 | 0 | 10 | 15503.0 |
| 6516.3 | 15341.9 | 2 | 0 | 9 | 15342.0 |
| 5945.7 | 16814.2 | 3 | 1 | 28 | 16819.7 |
| 5957.6 | 16780.6 | 3 | 1 | 27 | 16784.9 |
| 5968.3 | 16750.6 | 3 | 1 | 26 | 16744.3 |
| 5988.2 | 16694.9 | 3 | 1 | 25 | 16698.8 |
| 6007.6 | 16641.0 | 3 | 1 | 24 | 16647.1 |
| 6027.7 | 16585.5 | 3 | 1 | 23 | 16588.6 |
| 6052.8 | 16516.7 | 3 | 1 | 22 | 16519.6 |
| 6078.7 | 16446.3 | 3 | 1 | 21 | 16445.3 |
| 6110.1 | 16361.8 | 3 | 1 | 20 | 16362.4 |
| 6144.1 | 16271.3 | 3 | 1 | 19 | 16272.2 |
| 6181.7 | 16172.3 | 3 | 1 | 18 | 16173.7 |
| 6222.7 | 16065.8 | 3 | 1 | 17 | 16066.3 |
| 6266.9 | 15952.4 | 3 | 1 | 16 | 15952.1 |

Table 1. Magnetic Rotation Lines of $ICl^{35}$ with Corresponding Band Heads of its Absorption Spectrum (Continued)

| Wave-length in A. | Frequency in $cm^{-1}$ | Intensity* | Vibrational Assignment v" | v' | Absorption Band Heads** in $cm^{-1}$ |
|---|---|---|---|---|---|
| 6315.2 | 15830.4 | 2 | 1 | 15 | 15831.0 |
| 6367.0 | 15701.7 | 2 | 1 | 14 | 15702.5 |
| 6422.4 | 15566.2 | 2 | 1 | 13 | 15566.0 |
| 6481.9 | 15423.3 | 1 | 1 | 12 | 15424.5 |
| 6544.5 | 15275.8 | 1 | 1 | 11 | 15275.7 |
| 6611.4 | 15121.2 | 1 | 1 | 10 | 15121.4 |
| 6682.1 | 14961.2 | 1 | 1 | 9 | 14960.4 |

* Intensity was estimated visually by assigning the most intense line at 5941.8A the number 10.

** The band heads of the absorption spectrum for v" = 0 were taken from Darbyshire's paper (42), and those for v" = 1 were calculated by subtracting the constant increment 381.6 $cm^{-1}$ from the valves given for v" = 0.

Table 2. Magnetic Rotation Lines of $IC1^{37}$

| Wave-length | Frequency | Intensity | Vibrational Assignment v'' | v' | Absorption Band Heads* |
|---|---|---|---|---|---|
| 5785.7 A | 17279.2 $cm^{-1}$ | 1 | 0 | 31 | 17187.4 $cm^{-1}$ |
| 5793.2 | 17256.8 | 1 | 0 | 30 | 17188.7 |
| 5801.5 | 17232.1 | 1 | 0 | 29 | 17180.5 |
| 5817.1 | 17185.9 | 5 | 0 | 28 | 17163.0 |
| 5830.1 | 17147.6 | 5 | 0 | 27 | 17136.4 |
| 5844.6 | 17105.1 | 5 | 0 | 26 | 17100.8 |
| 5862.5 | 17052.9 | 5 | 0 | 25 | 17056.5 |
| 5880.3 | 17001.2 | 5 | 0 | 24 | 17003.6 |
| 5901.2 | 16941.0 | 5 | 0 | 23 | 16942.4 |
| 5925.8 | 16870.7 | 5 | 0 | 22 | 16873.0 |
| 5953.6 | 16791.9 | 4 | 0 | 21 | 16795.6 |
| 5983.5 | 16708.0 | 3 | 0 | 20 | 16710.4 |
| 6016.5 | 16614.4 | 3 | 0 | 19 | 16617.7 |
| 6052.8 | 16516.7 | 3 | 0 | 18 | 16517.5 |
| 6092.4 | 16409.4 | 2 | 0 | 17 | 16410.0 |
| 6134.8 | 16295.9 | 2 | 0 | 16 | 16295.5 |
| 6181.7 | 16172.3 | 3 | 0 | 15 | 16174.1 |
| 6230.7 | 16045.1 | 2 | 0 | 14 | 16046.1 |

*The band heads of the absorption spectrum were calculated from the equation (43),

$$\nu = 13558.0 + 205.26(v'+1/2) - 1.8649(v'+1/2)^2 - 0.03154(v'+1/2)^3$$

since $\rho = 0.9786$; $v'' = 0$; $W_e' = 205.26\ cm^{-1}$; $W_e'X_e' = 1.8649\ cm^{-1}$; $W_e'' = 375.96\ cm^{-1}$; $W_e''X_e'' = 1.4029\ cm^{-1}$; and $\nu_{el} = 13745.6\ cm^{-1}$.

It should be noted that deviations from this formula are to be expected in the range of very large v'.

Table 3. Isotope Effect in the Magnetic Rotation Lines of ICl

| Vibrational Assignment v" | v' | Frequency ($IC1^{35}$) | Frequency ($IC1^{37}$) | Isotope Effect (Observed) | Isotope Effect (Calculated)* |
|---|---|---|---|---|---|
| 0 | 31 | 17274.4 $cm^{-1}$ | 17279.2 $cm^{-1}$ | -4.8 $cm^{-1}$ | -10.8 $cm^{-1}$ |
| 0 | 30 | 17252.7 | 15256.8 | -4.1 | -4.1 |
| 0 | 29 | 17230.1 | 17232.1 | -2.0 | -2.2 |
| 0 | 28 | 17195.7 | 17185.9 | 9.8 | 7.8 |
| 0 | 27 | 17163.2 | 17147.6 | 15.6 | 12.9 |
| 0 | 26 | 17124.1 | 17105.1 | 19.0 | 17.5 |
| 0 | 25 | 17079.4 | 17052.9 | 26.5 | 21.6 |
| 0 | 24 | 17028.2 | 17001.2 | 27.0 | 25.2 |
| 0 | 23 | 16968.1 | 16941.0 | 27.0 | 28.3 |
| 0 | 22 | 16901.5 | 16870.7 | 30.8 | 31.0 |
| 0 | 21 | 16826.9 | 16791.9 | 35.0 | 33.2 |
| 0 | 20 | 16742.5 | 16708.0 | 34.4 | 35.0 |
| 0 | 19 | 16652.1 | 16614.4 | 37.7 | 36.2 |
| 0 | 18 | 16560.8 | 16516.7 | 44.1 | 37.1 |
| 0 | 17 | 16446.9 | 16409.4 | 37.5 | 37.7 |
| 0 | 16 | 16333.0 | 16295.9 | 37.1 | 37.9 |
| 0 | 15 | 16211.1 | 16172.3 | 38.8 | 37.7 |
| 0 | 14 | 16082.6 | 16045.1 | 37.5 | 37.1 |

*Isotope effect was calculated by the formula:

isotope effect = frequency ($IC1^{35}$)-frequency ($IC1^{37}$), where frequency ($IC1^{35}$) = $13553.9 + 209.75(v'+1/2) - 1.947(v'+1/2)^2 - 0.03366(v'+1/2)^3$, and frequency ($IC1^{37}$) = $13558.0 + 205.26(v'+1/2) - 1.8649(v'+1/2)^2 - 0.03154(v'+1/2)^3$.

Table 4. Unassigned Magnetic Rotation
Lines of ICl Believed due to Perturbation

| $\lambda$ | $\nu$ | Intensity | $\lambda$ | $\nu$ | Intensity |
|---|---|---|---|---|---|
| 5827.2 Å | 17156.2 $cm^{-1}$ | 4 | 5895.3 Å | 16958.0 $cm^{-1}$ | 4 |
| 5831.3 | 144.1 | 4 | 5898.3 | 949.4 | 4 |
| 5832.9 | 139.4 | 4 | 5903.6 | 934.1 | 4 |
| 5834.2 | 135.6 | 4 | 5910.0 | 915.8 | 4 |
| 5835.8 | 130.9 | 4 | 5912.7 | 908.1 | 4 |
| 5840.8 | 116.2 | 4 | 5919.0 | 890.1 | 4 |
| 5842.8 | 110.3 | 4 | 5922.7 | 876.5 | 4 |
| 5847.8 | 095.7 | 4 | 5930.3 | 857.9 | 4 |
| 5849.9 | 089.6 | 4 | 5933.3 | 849.4 | 4 |
| 5856.3 | 070.9 | 4 | 5937.4 | 837.7 | 4 |
| 5859.1 | 062.7 | 4 | 5950.8 | 799.8 | 3 |
| 5860.4 | 059.0 | 4 | 5962.7 | 766.3 | 2 |
| 5864.7 | 046.4 | 4 | 5963.6 | 763.8 | 2 |
| 5867.8 | 037.4 | 4 | 5965.8 | 757.6 | 2 |
| 5873.1 | 022.1 | 4 | 5976.1 | 728.7 | 3 |
| 5875.2 | 016.0 | 4 | 5978.8 | 721.1 | 3 |
| 5878.0 | 007.9 | 4 | 5981.1 | 714.7 | 3 |
| 5883.3 | 16992.6 | 4 | 5994.9 | 676.2 | 2 |
| 5885.3 | 986.8 | 4 | 5997.0 | 670.4 | 2 |
| 5887.3 | 981.0 | 4 | 5997.1 | 670.1 | 2 |
| 5889.8 | 973.8 | 4 | 5999.7 | 662.9 | 2 |

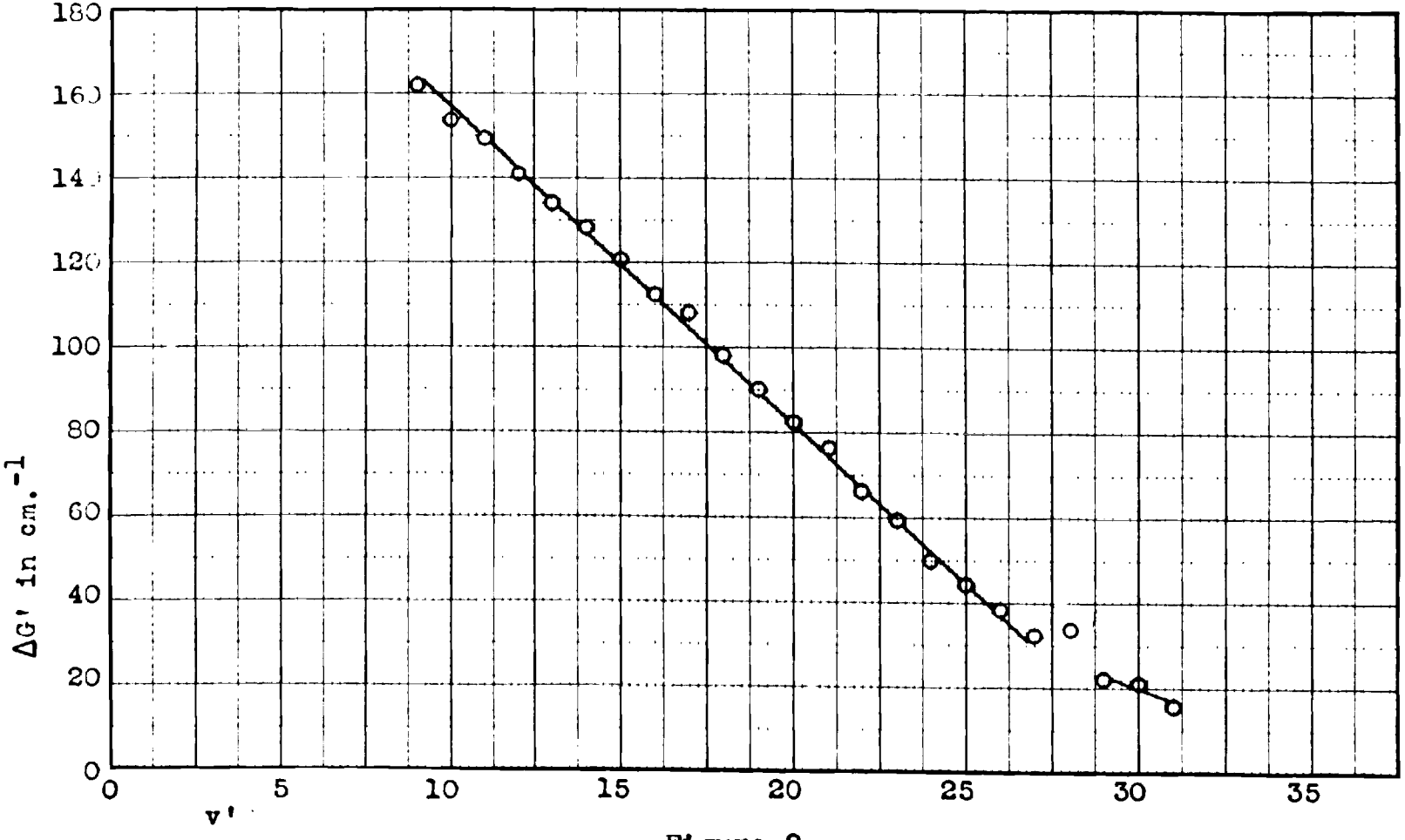


Figure 2

Separation of Successive Vibrational Bands, $\Delta G'(v')$, of $ICl^{35}$ from Its Magnetic Rotation Spectrum

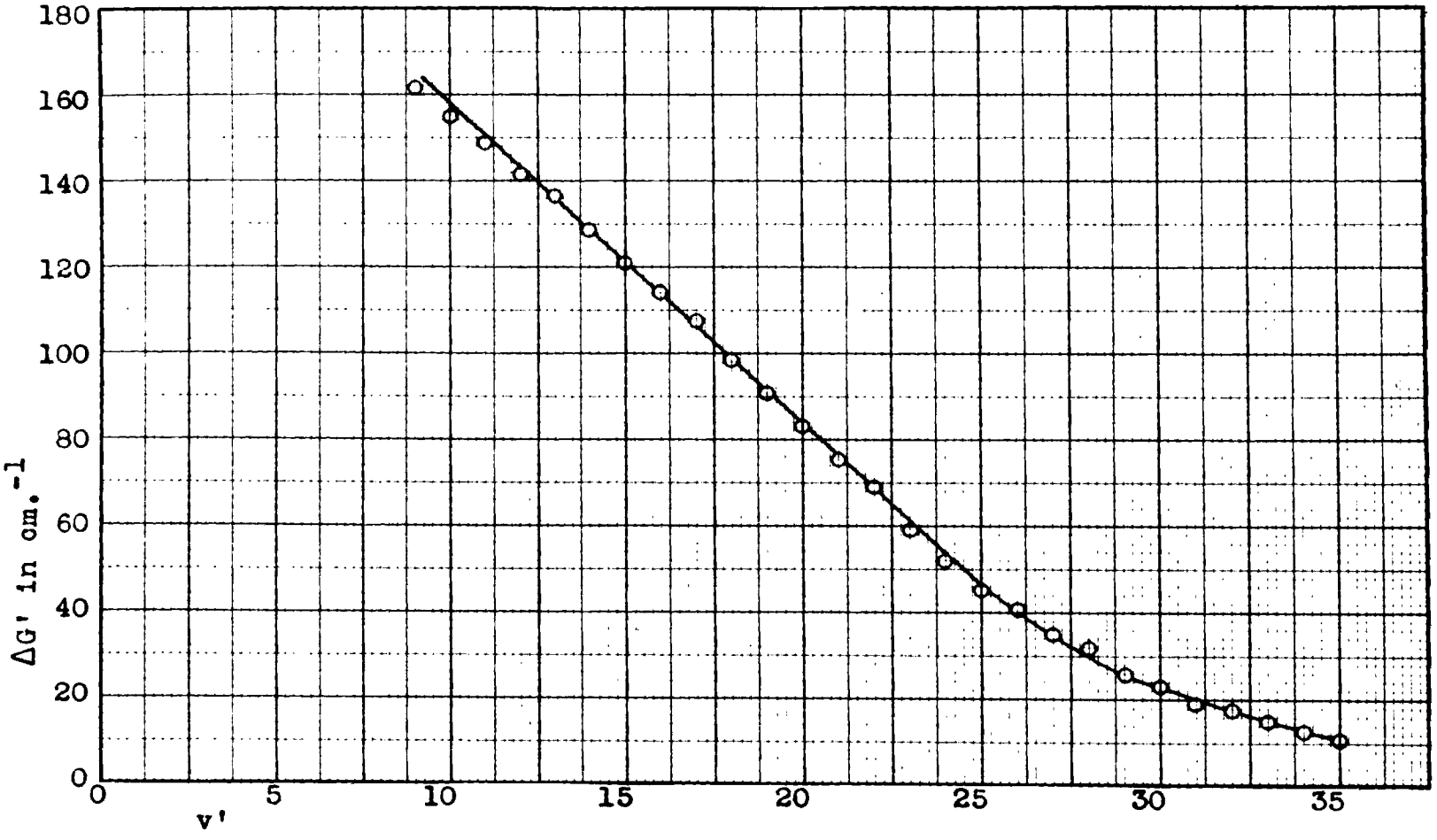


Figure 3

Separation of Successive Vibrational Bands, $\Delta G'(v')$, of $ICl^{35}$ from Its Absorption Spectrum (40)

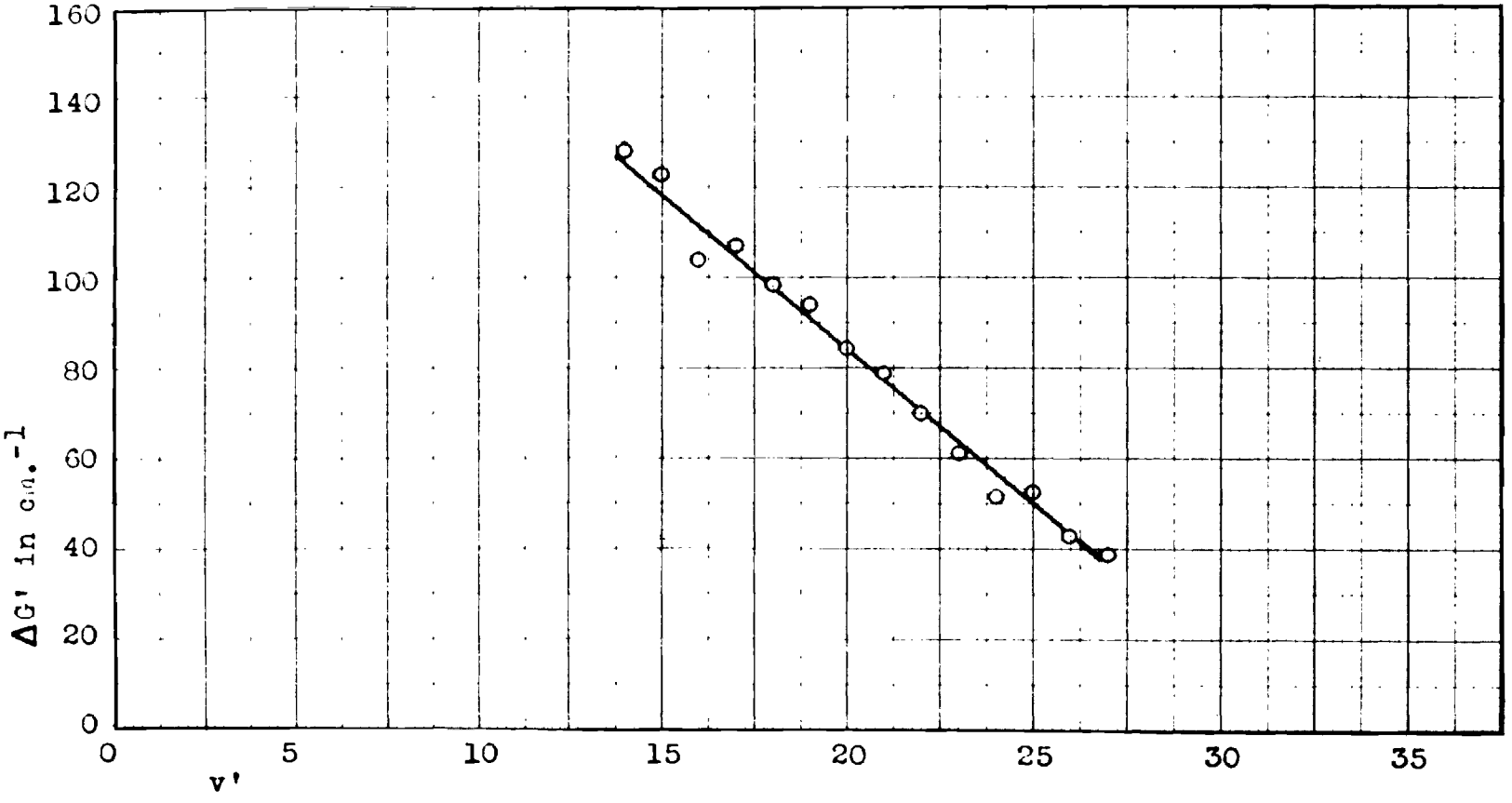


Figure 4

Separation of Successive Vibrational Bands, $\Delta G'(v')$, of $ICl^{37}$ from Its Magnetic Rotation Spectrum

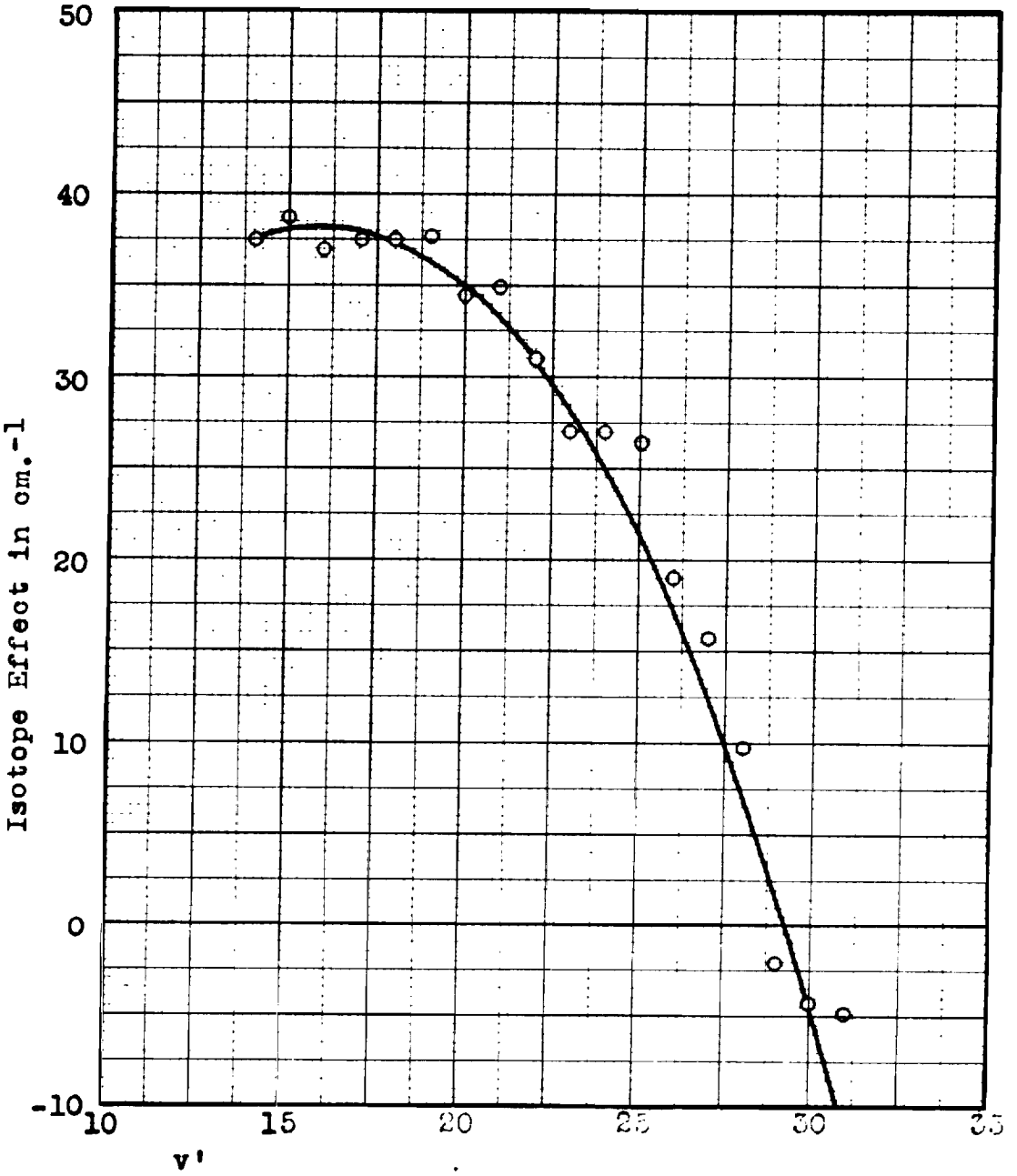


Figure 5

Isotope Effect in ICl from Its Magnetic Rotation Spectrum (Solid Curve Represents Values Calculated as Described in Table 2)

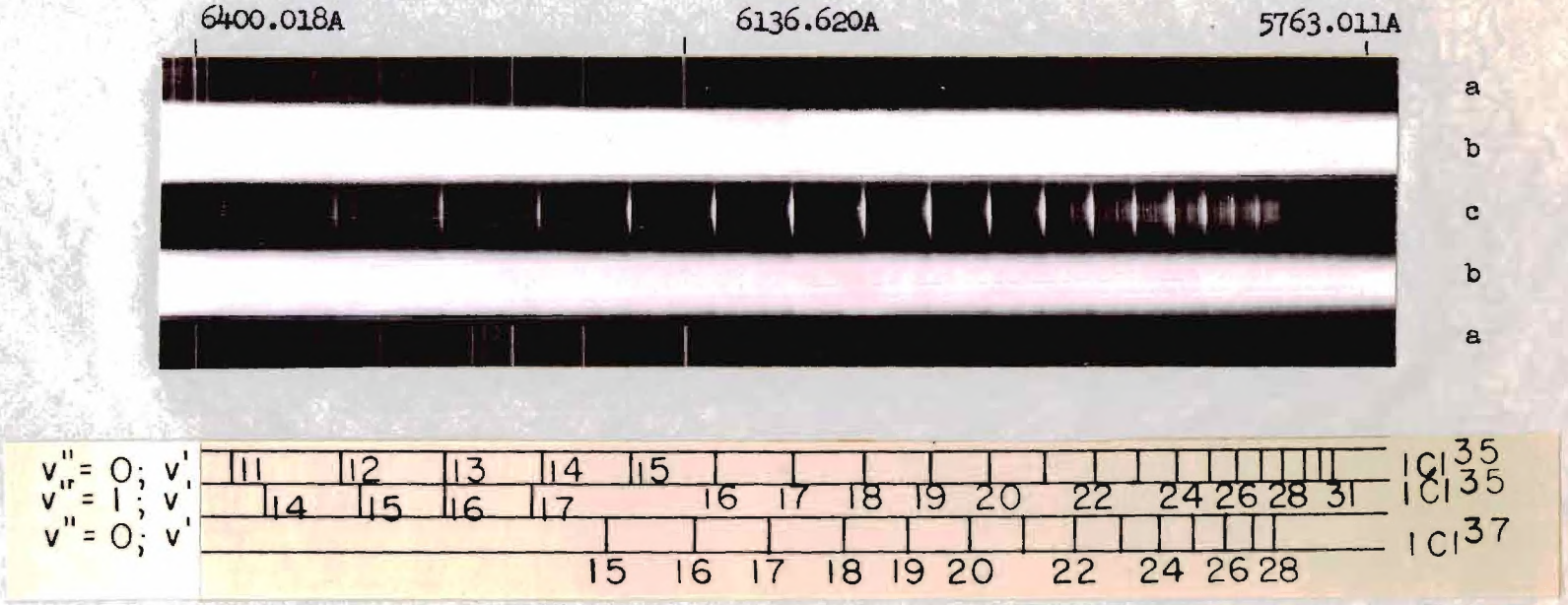


Figure 6

Magnetic Rotation Spectrum of ICl

(a) Iron Arc Spectrum

(b) Absorption Spectrum of ICl

(c) Magnetic Rotation Spectrum of ICl

states of diatomic halogen molecules and interhalogen compounds (39), and $1(^{1}\Pi)$ state, which dissociates into $^{2}P_{3/2}$ (I) and $^{2}P_{1/2}$ (Br), seems to be the most probable perturbing state.

The assignment of three bands to v" = 0, 1 and 2 gets further support from a study of the temperature effect. At 29°C, the v" = 0 band is found more intense than the v" = 2 band, while at 50°C, the v" = 2 band is more intense. In both cases, the v" = 1 band is the most intense. This temperature effect can be explained by the population of IBr molecules in v" = 0, 1 and 2 levels. The relative population is very sensitive to temperature.

The two maxima in each band may be due to different isotopic species, $IBr^{79}$ and $IBr^{81}$. In order to prove that point, $IBr^{79}$ and $IBr^{81}$ were prepared from $Br^{79}Br^{79}$ and $Br^{81}Br^{81}$ respectively. Because of the very limited quantities of isotopically enriched bromine available and the possible loss through reactivity of IBr with the stopcock grease, only short-time exposures were utilized. These short exposures necessitated a 1 mm slit width and consequent loss of detail. However, when these spectra were compared with the magnetic rotation spectrum of IBr which had been prepared from natural bromine and contained $IBr^{79}$ and $IBr^{81}$ in equal abundance (Figure 9), it was found possible to assign certain lines to $IBr^{79}$ and $IBr^{81}$ separately. Other lines appeared in the region where the magnetic rotation spectra of $IBr^{79}$ and $IBr^{81}$ coexisted. All the magnetic rotation lines and their assignments to different isotopic species are listed in Table 5.

When the magnetic rotation spectrum of IBr is compared with its absorption spectrum, it is noticed that the magnetic rotation lines

with maximum intensity are very close to the band heads of the absorption spectrum (41) and thus have low J values. This gives additional support to the assumption that the upper state $0^+$ is perturbed by a $1(\,'\pi\,)$ state. Since one of the selection rules for pertubation is that both states must have the same total angular momentum J, the perturbing state must give a higher Verdet constant for low J values than that for high J values. The $1(\,'\pi\,)$ state has this property as shown by the formula (8).

Vibrational assignments could be made for the magnetic rotation lines of IBr and are listed in Table 5. It was noted that the vibrational level of the upper state is mainly $v' = 25$ for $IBr^{81}$ and $v' = 26$ for $IBr^{79}$. In Table 6, separations between adjacent vibrational levels of the ground state were calculated for the two cases, and found to be in good agreement with the calculated values of $\Delta G_{v''+1/2}$.

It seems necessary to explain why the pertubation occurs at different vibrational levels of the upper state $0^+$ for $IBr^{79}$ and $IBr^{81}$. If the explanation in terms of a perturbing state is valid, it may be possible to learn something about the properties of the perturbing state. Five pairs of magnetic rotation lines of IBr can be identified with $IBr^{79}$ and $IBr^{81}$ correspondingly and are listed in Table 7 with the isotope effects of the upper state calculated as shown there. It is encouraging that the values agree within experimental error. This isotopic effect may be the isotopic shift of either the perturbed state $0^+$ or the perturbing state $'\pi$. But both states are expected to give isotopic shifts of only a few wave numbers and an isotopic shift of 33.7 $cm^{-1}$ is too big for either of these states. It seems more reasonable to assume that the isotopic effect is due to the separation between the adjacent vibrational levels of the perturbing state $1(\,'\pi\,)$.

It is probable that two adjacent vibrational levels of the state 1 are perturbing $v' = 26$ of the state $0^+$ for $IBr^{79}$ and $v' = 25$ for $IBr^{81}$ respectively. The isotopic shifts in the 1 and $0^+$ states may be different from each other in such a way that the lower vibrational level of the 1 state perturbs $v' = 25$ of the $0^+$ state for $IBr^{81}$ and the higher vibrational level of $1(\,'\pi\,)$ state pertrubs $v' = 26$ of $0^+$ state for $IBr^{79}$. The 1 state is a state with a shallow minimum in its potential curve. It seems very probable that the vibrational levels concerned have low v values. If this is true and one assumes $W_eX_e$ to be small, then the separation between adjacent vibrational levels gives the value of $W_e$ of the state.

$$\Delta G_{v + 1/2} = W_e - 2W_eX_e - 2W_eX_e \approx W_e.$$

Hence the 1 state has the value of $W_e$ equal to 33.7 $cm^{-1}$.

As the absorption spectra of $IBr^{79}$ and $IBr^{81}$ were easily obtained for the transition $0^+ \leftarrow {}'\Sigma^+$, it was possible to measure the vibrational isotopic shifts which are listed in Table 8. But, due to the diffuseness of the band heads and the limitations of the equipment, the isotopic shifts are not believed to be accurate in the first decimal place.

Bromine.--As early as 1912, Ribaud reported the magnetic rotation spectrum of bromine vapor (47). He succeeded in pointing out that the green magnetic rotation spectrum of bromine was not due to the longitudinal Zeeman effect, as he could not find any modification of the absorption lines when bromine was placed in a longitudinal magnetic field of 24,000 gauss. But he did not suggest any feasible theory for the

Table 5. Magnetic Rotation Spectrum of IBr

| Magnetic Rotation Lines | Vibrational Assignment v'' | v' | Intensity | Isotopic Species | |
|---|---|---|---|---|---|
| 18040.1 $cm^{-1}$ | 0 | 25 | | $IBr^{81}$ | |
| 18045.9 | 0 | 25 | | $IBr^{81}$ | |
| 18050.4 | 0 | 25 | | $IBr^{81}$ | |
| 18053.0 | 0 | 25 | | $IBr^{81}$ | |
| 18059.2 | 0 | 25 | | $IBr^{81}$ | |
| 18064.1 | 0 | 25 | | $IBr^{81}$ | |
| 18067.7 | 0 | 25 | | $IBr^{81}$ | |
| 18073.0 | 0 | 25 | Maximum | $IBr^{81}$ | |
| 18078.7 | 0 | 26 | | $IBr^{81}$ | $IBr^{79}$ |
| 18083.5 | 0 | 26 | | $IBr^{81}$ | $IBr^{79}$ |
| 18086.3 | 0 | 26 | | $IBr^{81}$ | $IBr^{79}$ |
| 18091.6 | 0 | 26 | | | $IBr^{79}$ |
| 18095.8 | 0 | 26 | | | $IBr^{79}$ |
| 18101.7 | 0 | 26 | | | $IBr^{79}$ |
| 18105.3 | 0 | 26 | Maximum | | $IBr^{79}$ |
| 18110.3 | 0 | 27 | | | $IBr^{79}$ |
| 18114.0 | 0 | 27 | | | $IBr^{79}$ |
| 18117.8 | 0 | 27 | | | $IBr^{79}$ |
| 18121.4 | 0 | 27 | | | $IBr^{79}$ |
| 18128.0 | 0 | 27 | | | $IBr^{79}$ |
| 18131.3 | 0 | 27 | | | $IBr^{79}$ |
| 17780.3 | 1 | 25 | | $IBr^{81}$ | |
| 17785.2 | 1 | 25 | | $IBr^{81}$ | |
| 17790.1 | 1 | 25 | | $IBr^{81}$ | |
| 17795.6 | 1 | 25 | | $IBr^{81}$ | |
| 17799.7 | 1 | 25 | | $IBr^{81}$ | |
| 17803.5 | 1 | 25 | Maximum | $IBr^{81}$ | |
| 17808.2 | 1 | 26 | | $IBr^{81}$ | $IBr^{79}$ |
| 17811.2 | 1 | 26 | | $IBr^{81}$ | $IBr^{79}$ |
| 17815.3 | 1 | 26 | | $IBr^{81}$ | $IBr^{79}$ |
| 17818.8 | 1 | 26 | | $IBr^{81}$ | $IBr^{79}$ |
| 17824.5 | 1 | 26 | | | $IBr^{79}$ |
| 17830.5 | 1 | 26 | | | $IBr^{79}$ |
| 17835.0 | 1 | 26 | Maximum | | $IBr^{79}$ |
| 17838.5 | 1 | 27 | | | $IBr^{79}$ |
| 17842.9 | 1 | 27 | | | $IBr^{79}$ |
| 17845.2 | 1 | 27 | | | $IBr^{79}$ |
| 17846.1 | 1 | 27 | | | $IBr^{79}$ |
| 17852.8 | 1 | 27 | | | $IBr^{79}$ |

Table 5. Magnetic Rotation Spectrum of IBr
(Continued)

| Magnetic Rotation Lines | Vibrational Assignment v'' | Vibrational Assignment v' | Intensity | Isotopic Species | |
|---|---|---|---|---|---|
| 17508.3 | 2 | 25 | | $IBr^{81}$ | |
| 17538.2 | 2 | 25 | Maximum | $IBr^{81}$ | |
| 17552.2 | 2 | 26 | | $IBr^{81}$ | $IBr^{79}$ |
| 17569.8 | 2 | 26 | Maximum | $IBr^{81}$ | $IBr^{79}$ |
| 17571.4 | 2 | 27 | | $IBr^{81}$ | $IBr^{79}$ |
| 17592.7 | 2 | 27 | | | $IBr^{79}$ |

Table 6. Separation between the Vibrational Levels of the Ground State from the Magnetic Rotation Spectrum of IBr

| v' | v" | Magnetic Rotation Lines of Maximum Intensity | Separation between adjacent vibrational levels of the ground state | $\Delta G^*_{v''+1/2}$ |
|---|---|---|---|---|
| 26 | 0 | 18105.3 $cm^{-1}$ | | |
| 26 | 1 | 17835.0 | 270.3 $cm^{-1}$ | 266.8 $cm^{-1}$ |
| 26 | 2 | 17569.8 | 265.2 | 265.2 |
| 25 | 0 | 18073.0 | | |
| 25 | 1 | 17803.5 | 269.5 | 266.8 |
| 25 | 2 | 17538.2 | 265.3 | 265.2 |

$^*\Delta G_{v''+1/2} = W_e'' - 2W_e''X_e'' - 2W_e'' X_e'' v''$

where $W_e'' = 268.4\ cm^{-1}$; $W_e''X_e'' = 0.78\ cm^{-1}$ (46).

Table 7. Isotopic Effect from the Magnetic Rotation Spectrum of IBr

| Vibrational Assignment of $^1\Sigma^+$ v" | Corresponding Magnetic Rotation Lines $IBr^{79}$ | $IBr^{81}$ | $\Delta\nu$ | $\Delta\nu''$ | $\Delta\nu'$ |
|---|---|---|---|---|---|
| 0 | 18105.3 $cm^{-1}$ | 18073.0 $cm^{-1}$ | 32.3 | 1.0 | 33.3 |
| 0 | 18091.6 | 18059.2 | 32.4 | 1.0 | 33.4 |
| 1 | 17838.5 | 17808.2 | 30.3 | 3.0 | 33.3 |
| 1 | 17835.0 | 17803.5 | 31.5 | 3.0 | 34.5 |
| 1 | 17830.5 | 17799.7 | 30.8 | 3.0 | 33.8 |
| | | | | Mean | 33.7 |

Note: $\Delta\nu$ = observed difference in wave numbers between the corresponding magnetic rotation lines of $IBr^{79}$ and $IBr^{81}$.

$\Delta\nu''$ = calculated isotopic shift for the ground state.

$\Delta\nu'$ = isotopic effect in the upper state.

$\Delta\nu'' = (1-\rho)\, W_e''(v'' + 1/2) - (1-\rho^2)\, W_e''X_e''(v'' + 1/2)^2$

$\rho = \sqrt{\frac{\mu}{\mu'}} = 0.98477 = 0.99236$

$\mu = 48.70388$ for $IBr^{79}$

$\mu' = 49.45673$ for $IBr^{81}$

$W_e'' = 268.4\ cm^{-1}$

$W_e''X_e'' = 0.78\ cm^{-1}$

$\Delta\nu' = \Delta\nu + \Delta\nu''$.

Table 8. Isotopic Shifts in the Absorption Spectrum of IBr for the $0^+ \leftarrow {}^1\Sigma^+$ Transition

| v'' | v' | Isotopic Shifts* | v'' | v' | Isotopic Shifts* |
|---|---|---|---|---|---|
| 0 | 29 | +0.76 $cm^{-1}$ | 1 | 28 | +1.63 $cm^{-1}$ |
| 0 | 28 | 1.88 | 1 | 27 | 1.23 |
| 0 | 27 | 1.30 | 1 | 26 | -- |
| 0 | 26 | -- | 1 | 25 | 1.45 |
| 0 | 25 | -- | 1 | 24 | 1.34 |
| 0 | 24 | 1.45 | 1 | 23 | 1.85 |
| 0 | 23 | 1.12 | 2 | 28 | +2.03 $cm^{-1}$ |
| | | | 2 | 27 | 1.63 |

*Isotopic shifts are the differences between the frequencies (in wave numbers) of the corresponding band heads of $IBr^{79}$ and $IBr^{81}$: i.e.

$$\text{Isotopic Shifts} = \nu(IBr^{79}) - \nu(IBr^{81})$$

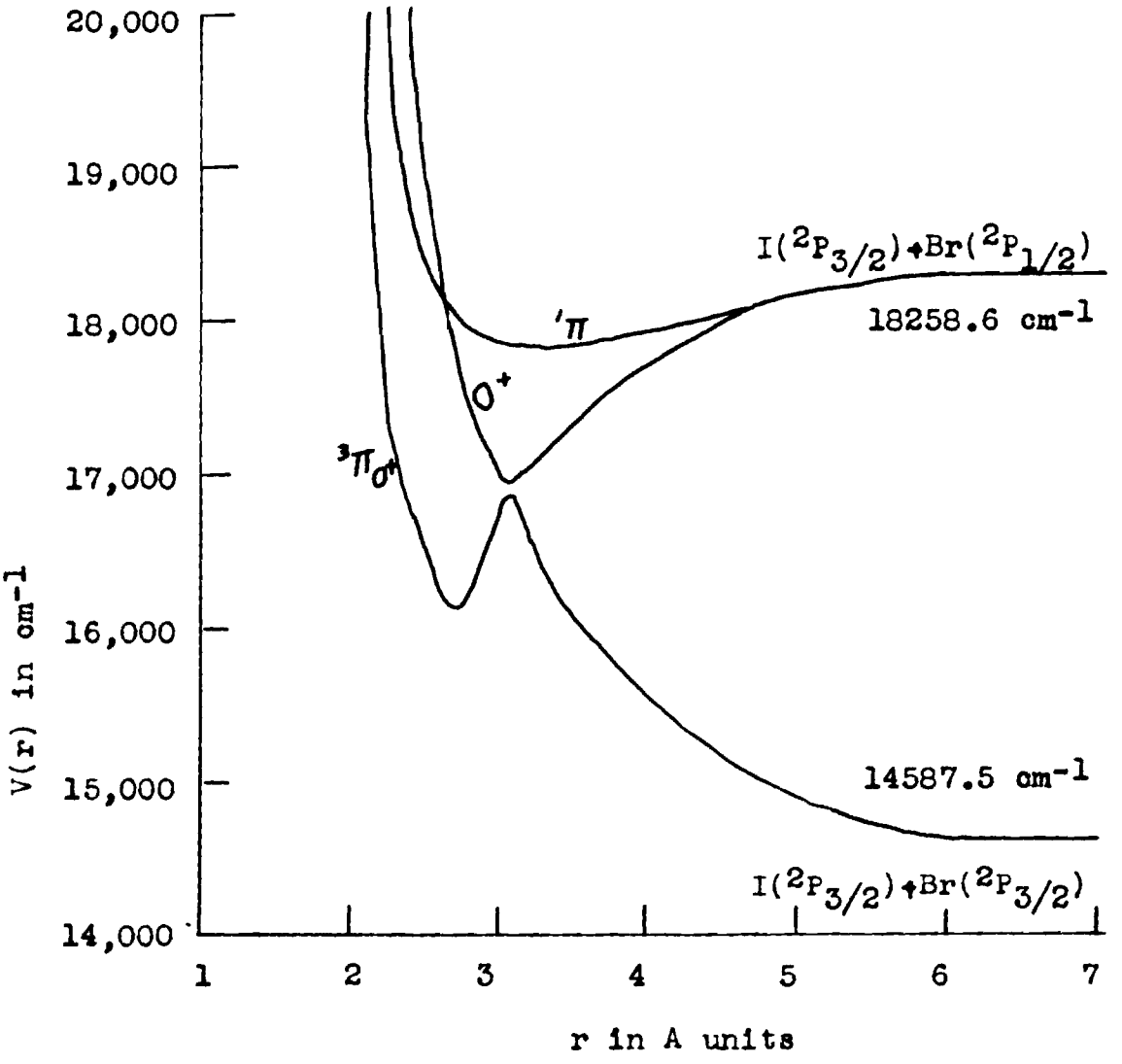


Figure 7

Approximate Potential Energy Curves, V(r), for $IBr^{79}$. The Ground state $^1\Sigma^+$ is omitted here.

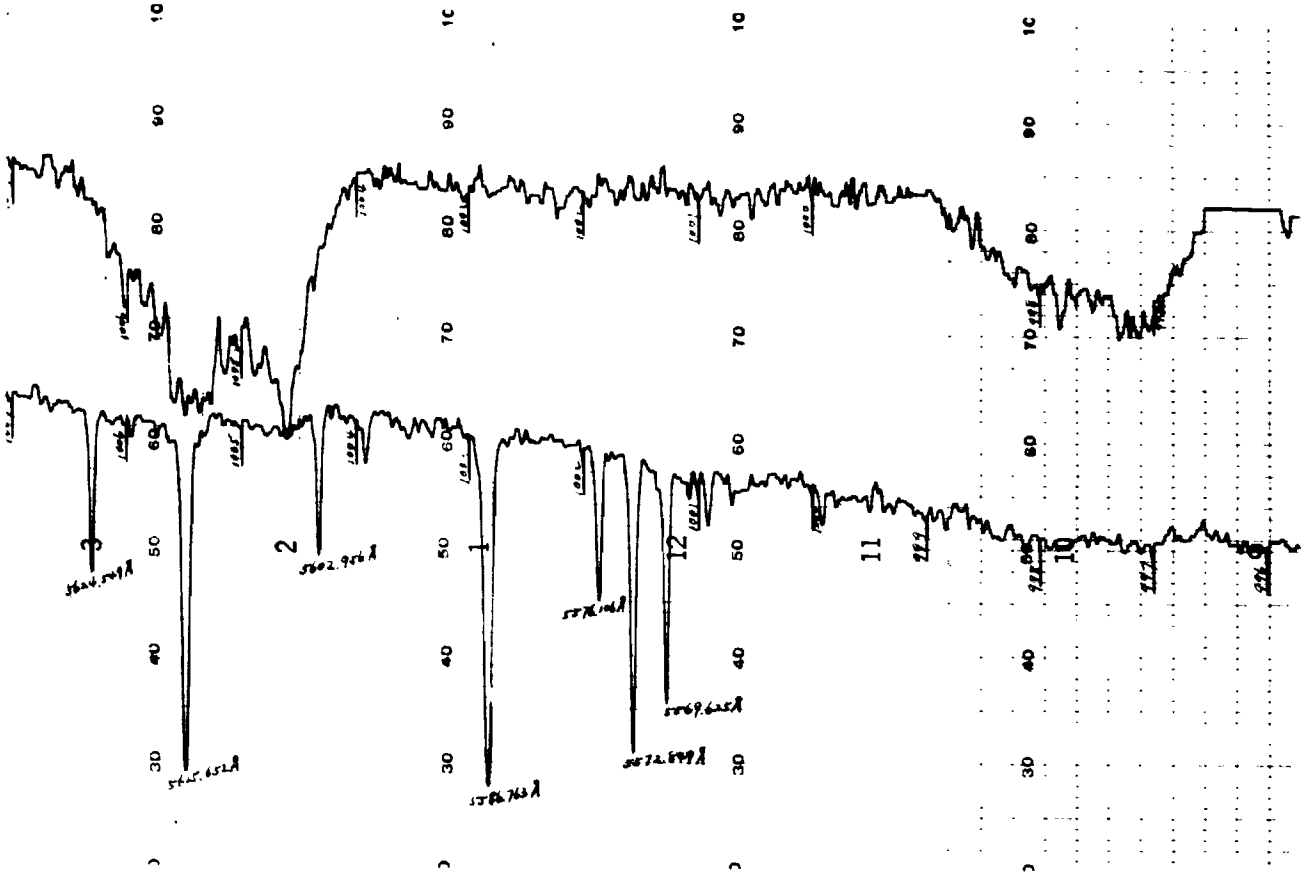

Figure 8

Microphotometric Tracing of the Magnetic
Rotation Spectrum of IBr

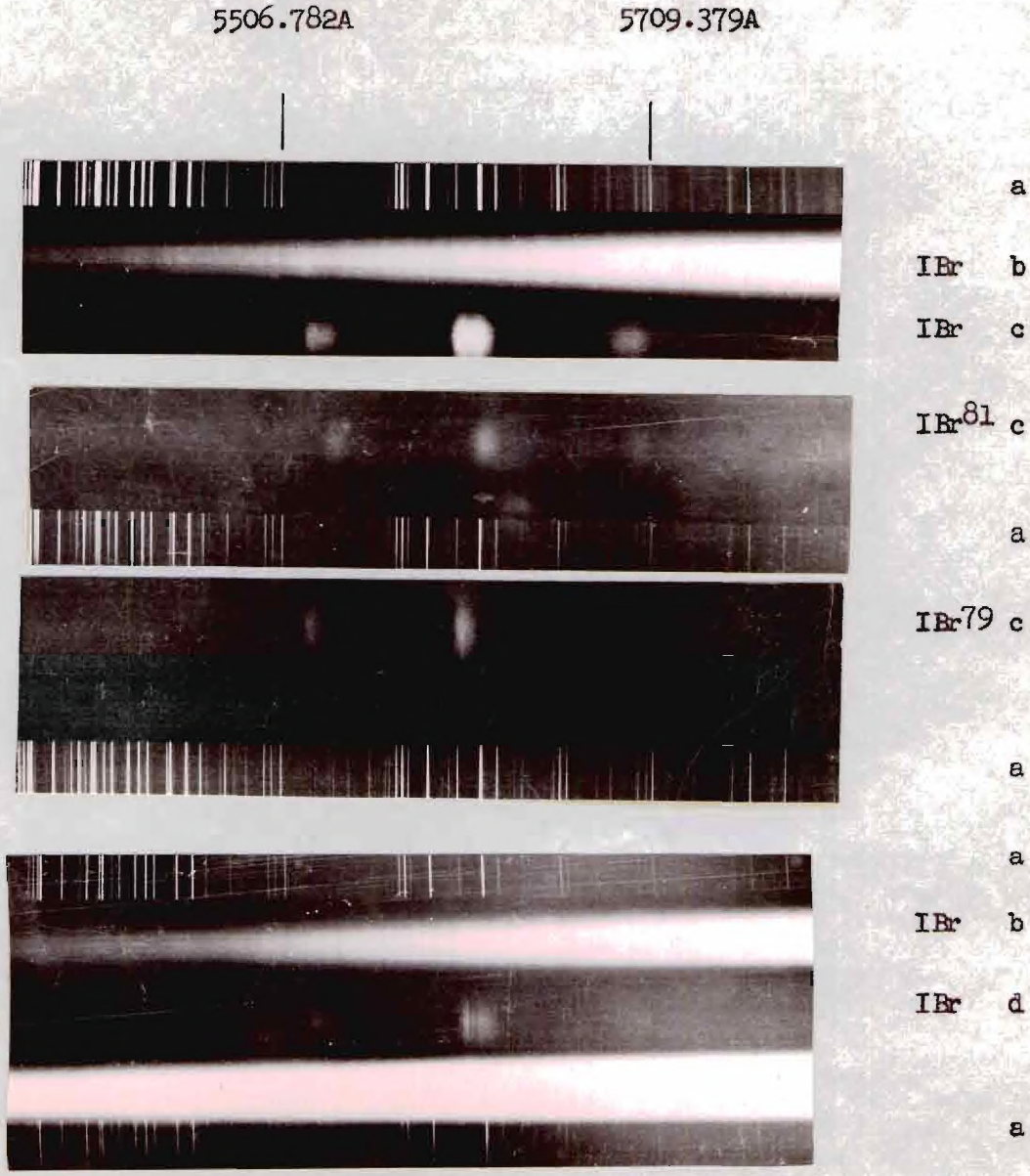


Figure 9

Magnetic Rotation Spectrum of IBr

(a) Iron Arc Spectrum; (b) Absorption Spectrum; (c) Magnetic Rotation Spectrum; and (d) Fine Structure of Magnetic Rotation Spectrum.

appearance of the magnetic rotation spectrum. It is with this aim that the present investigation of bromine was started.

Bromine was found to give a green magnetic rotation spectrum which consisted of hundreds of fine lines. With the equipment available, about 132 lines between 5110A and 5370A were measured and are listed in Table 9. As the spectrograph had a dispersion of 10.9 A/mm and a slit width of 60 microns was used, the instrument was able to resolve lines at 0.6A apart. But the width of the magnetic rotation lines might be much smaller than 0.6A, and so each of the lines in Table 7 might actually consist of several sharp lines.

During the photographing of the magnetic rotation spectrum of bromine, several peculiar phenomena were observed which led to studies of the temperature effect, the pressure effect, and the effect of of foreign gases. With the same vapor pressure (say 11.4 mm) of bromine, the magnetic rotation spectrum was photographed separately when the gas was kept at 137°C, 30°C, and -15°C. It was found that different temperatures gave different intensity of the magnetic rotation lines in region I between 5110A and 5190A, and in region II between 5190A and 5370A. At 137°C, the lines appeared very intense in region II and quite faint in region I; at 30°C, they had about equal intensity in both regions; while at -15°C, the lines in region I appeared to be more intense than those in region II.

These observations on the temperature effect can be explained by a change in the population of the bromine molecules in the vibrational levels of the ground electronic state. At -15°C, the most molecules are in the $v'' = 0$ vibrational level which will give intense

magnetic rotation lines in the region I. As the temperature increases, the population in v" = 1 level is increased. The continuum of the v" = 1 level starts at 19264 $cm^{-1}$ or 5189.6A and it is known that bromine absorbs very strongly in the continuum. This absorption in the continuum diminishes the intensity of the magnetic rotation lines in region I, while the increase of population in the v" = 1 level increases the intensity of the lines in region II. At 30°C, the two effects are balanced against each other such that the spectrum has about equal intensity in the two regions, while at 137°C, the bromine molecules in the v" = 1 level absorb nearly all the restored light in region I, and give rather intense lines in region II.

With the temperature kept constant (say 20°C), the pressure effect was studied by photographing the magnetic rotation spectrum of bromine at various vapor pressures. Results showed that at a pressure of 1.83 mm, the spectrum appeared to be quite faint; at 4.77 mm, it was more intense than the previous one in the whole region between 5110A and 5370A; at 11.4 mm, the lines appeared more intense in region II and less intense in region I than those at 4.77 mm; at 25.2 mm, the lines were very faint in region I and much less intense in region II than those at 11.4 mm; and at 50.5 mm or higher pressures the whole magnetic rotation spectrum disappeared.

The pressure effect can be explained by a combination of two factors: the population and the pertubation factors. The first one is that increasing the pressure of bromine gas increases the actual number of molecules in v" = 1, 2, and so on. The continua from the higher vibrational levels of the ground state start at wave lengths longer than the convergence limit 19585 $cm^{-1}$ or 5104.5A. Since bromine

has the highest extinction coefficients in the continuum for the transition $0^+_u \leftarrow {}^1\Sigma^+_g$ the light coming through the crossed Ahrens polarizing prisms for the magnetic rotation spectrum is absorbed by the continua of higher vibrational levels whose actual population becomes greater as the pressure of bromine gas increases. The second factor is that increasing the pressure increases the number of bromine molecules present in the optical cell resulting in increased molecular collisions. These collisions may relax the selection rule ($g \not\leftrightarrow u$) on perturbation and cause a mixing of the upper state $0^+_u({}^3\Pi)$ with a replusive state $0^+_g$ (48). This perturbation causes predissociation of the visible spectrum of bromine and destroys its magnetic rotation spectrum. It may be of interest to point out that the corresponding predissociation has been found in the visible absorption spectra of ICl and IBr where the selection rule ($g \not\leftrightarrow u$) is not valid.

The presence of foreign gases will give collisions required for the predissociation without changing the actual population in the vibrational levels. Thus we would expect that the magnetic rotation spectrum as a whole would diminish in intensity as the pressure of the foreign gas increases. This was confirmed by experiments with argon and helium as foreign gases (Figure 11). With the partial pressure of bromine kept at 7.45 mm, argon was introduced into the optical cell from a cylinder. When the partial pressure of argon reached 50 mm, the magnetic rotation spectrum of bromine was photographed. It was photographed again when the partial pressure of argon was at 210 mm. It was found that the presence of argon diminished the intensity of the magnetic rotation spectrum of bromine rapidly. The

spectrum with argon at a partial pressure of 50 mm was much fainter than that of the pure bromine gas. The spectrum completely disappeared when the partial pressure of argon reached 210 mm. The same experiments were carried out with helium as the foreign gas with similar results. It was also noticed that the magnetic rotation spectrum of bromine with 50 mm of helium was fainter than that with 50 mm of argon. All these results can be explained by the collision-pertubation of the $0^+_u(^3\Pi)$ state with a repulsive $0^+_g$ state.

The absorption and magnetic rotation spectra of $Br_2$ appear to be very complex, as shown in Figure 11, because the spectra of $Br^{79}Br^{79}$, $Br^{79}Br^{81}$ and $Br^{81}Br^{81}$ which occur naturally in the ratio 1:2:1 overlap each other. Brown has measured the frequencies of band heads in the main system ($0^+_u \leftarrow {}^1\Sigma^+$) of the absorption spectrum of bromine (49). During the present investigation, the frequencies of the magnetic rotation lines were measured and are listed in Table 9. It was found that there was hardly any correlation between the absorption and magnetic rotation spectra of bromine. This lack of correlation can also be seen from Figure 11.

Because of the very great complexity of this spectrum, the only feasible way to attack the problem seemed to be through a study of the absorption and magnetic rotation spectra of $Br^{79}Br^{79}$ and $Br^{81}Br^{81}$ separately. Fortunately we were able to get these two isotopic species of bromine from the Atomic Energy Commission through the Oak Ridge National Laboratory. Photographs of the absorption and magnetic rotation spectra of $Br^{81}Br^{81}$ are shown on Figure 12, and those of $Br^{79}Br^{79}$ on Figure 13. Both photographs show the same kind of correlation

between the absorption and magnetic rotation spectra: that is, magnetic rotation lines are absent at the band heads of the absorption spectrum. As the spectrum is shaded toward the red, absorption lines become weaker toward wave lengths to the red of the band head in each band, and appear bright on the photographs. The magnetic rotation lines in each band appear to be stronger in the region at wave lengths greater than the band head, which implies that in each band magnetic rotation lines are absent at $J = 0$, weak at low J values, and strong at high J values. This phenomenon agrees very well with the formula (12) for rotational distortion. In this formula, the Verdet constant is proportional to the factor $J'(J'+1)(e^{-\frac{W_{J'\pm1}}{KT}})$, which is zero when $J = 0$, small for low J values and large for high J values. Hence it seems very probable that the magnetic rotation spectra of $Br^{79}Br^{79}$ and $Br^{81}Br^{81}$ are due to rotational distortion. This assignment gets more support when the absorption and magnetic rotation spectra of $I_2$ are compared in Figure 10. $I_2$ is known to give its magnetic rotation spectrum because of rotational distortion (30). The correlation between the absorption and magnetic rotation spectra of the isotopic species of bromine is very obvious and is the same as that between these spectra of $I_2$. Unfortunately, the spectrum appears so complex as to prevent a complete analysis of the magnetic rotation spectra of $Br_2$ and $I_2$ with available equipment.

The absorption spectra of $Br_2$ and IBr in the infrared region have been assigned to the $^3\Pi_1 \leftarrow {}^1\Sigma^+$ transition, which should give a magnetic rotation spectrum as in the case of ICl. A search for the magnetic rotation spectra of $Br_2$ and IBr was made with the present

set-up, using Eastman type 1 N film, but none was found in the infrared region. This negative result may be explained by one of the following reasons:

(1) the assignment of the transition $^3\Pi_1 \leftarrow {}^1\Sigma^+$ is in error, and it may be $0^- \leftarrow {}^1\Sigma^+$ as suggested by Brown (50).

(2) the line width of the absorption spectrum is broader than the normal Zeeman splitting, since the infrared spectra of $Br_2$ and IBr are diffuse; or

(3) the magnetic rotation spectra may be absorbed by the molecules when they have high extinction coefficients in the region.

The last point is known for the green magnetic rotation spectrum of bromine. But both bromine and iodine monobromide have weak absorption spectra in the infrared region, and this is not likely the reason. The second point may be a very feasible one. Further experiments with lower vapor pressures of bromine and iodine monobromide in a much longer optical cell are needed to confirm this point. The first point is also very possible. Questions have been raised as to why the infrared absorption spectrum, if it belongs to the $^3\Pi_1 \leftarrow {}^1\Sigma^+$ transition, is so weak since it is allowed by the selection rule for case (c) coupling. Although Van Vleck (51) has worked out a reason for this weak absorption spectrum, it does not rule out the possibility that the weak spectrum may be due to a forbidden transition like $0^- ({}^3\Pi) \leftarrow {}^1\Sigma^+$. Thus either the diffuseness of the absorption spectrum or the wrong assignment of the transition may be the reason that no infrared magnetic rotation spectrum has been found for $Br_2$ and IBr.

Table 9. Magnetic Rotation Spectrum of $Br_2$

| Wave-lengths | Wave-lengths | Wave-lengths |
|---|---|---|
| 5125.4 Å | 5173.7 Å | 5216.6 Å |
| 5128.9 | 5175.9 | 5218.3 |
| 5131.7 | 5179.3 | 5220.0 |
| 5133.0 | 5181.3 | 5222.7 |
| 5135.3 | 5183.2 | 5224.6 |
| 5136.6 | 5184.3 | 5226.8 |
| 5139.4 | 5185.7 | 5228.3 |
| 5142.3 | 5186.9 | 5229.2 |
| 5144.0 | 5188.6 | 5231.3 |
| 5145.3 | 5190.7 | 5233.6 |
| 5147.1 | 5192.5 | 5235.1 |
| 5150.9 | 5194.3 | 5237.4 |
| 5153.1 | 5196.0 | 5239.6 |
| 5155.2 | 5197.5 | 5240.6 |
| 5156.4 | 5199.7 | 5241.8 |
| 5157.6 | 5201.3 | 5242.9 |
| 5160.0 | 5202.9 | 5244.5 |
| 5163.8 | 5204.5 | 5246.0 |
| 5165.9 | 5206.9 | 5247.9 |
| 5167.6 | 5208.7 | 5250.3 |
| 5170.9 | 5210.9 | 5250.3 |
| 5172.8 | 5213.4 | 5252.8 |
| 5255.0 | 5299.0 | 5335.9 |
| 5257.3 | 5301.5 | 5338.0 |
| 5258.6 | 5302.9 | 5340.3 |
| 5262.0 | 5304.2 | 5343.1 |
| 5263.6 | 5304.8 | 5344.4 |
| 5264.7 | 5307.0 | 5347.3 |
| 5265.7 | 5308.3 | 5351.7 |
| 5268.6 | 5309.4 | 5352.7 |
| 5270.0 | 5311.2 | 5354.8 |
| 5271.6 | 5314.7 | 5357.8 |
| 5272.8 | 5317.6 | 5359.0 |
| 5276.1 | 5319.5 | 5361.6 |
| 5278.7 | 5322.4 | 5365.7 |
| 5281.0 | 5324.5 | 5367.5 |

Table 9. Magnetic Rotation Spectrum of $Br_2$
(Continued)

| Wave-lengths | Wave-lengths | Wave-lengths |
|---|---|---|
| 5284.0 Å | 5326.3 Å | 5368.9 Å |
| 5286.0 | 5327.9 | 5371.6 |
| 5287.9 | 5329.2 | 5373.7 |
| 5289.0 | 5330.2 | 5374.4 |
| 5290.8 | 5331.4 | 5376.0 |
| 5293.4 | 5332.4 | 5377.7 |
| 5294.8 | 5333.2 | 5379.3 |
| 5296.4 | 5335.1 | 5383.2 |

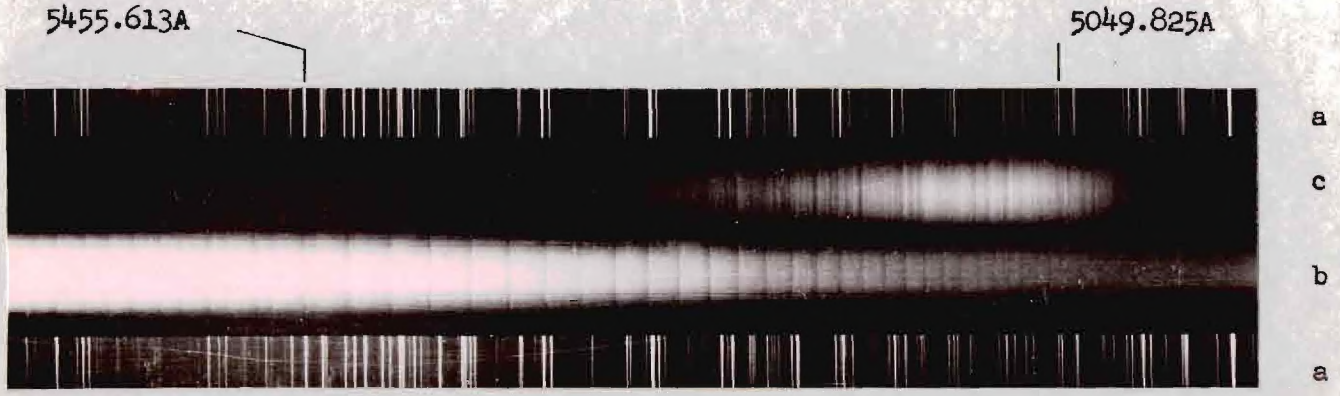


Figure 10

Magnetic Rotation Spectrum of Iodine

with a, b and c same as in Figure 9.


Figure 11

Magnetic Rotation Spectrum of $Br_2$

and the Effect of Foreign Gases

with a, b, and c same as in Figure 9.

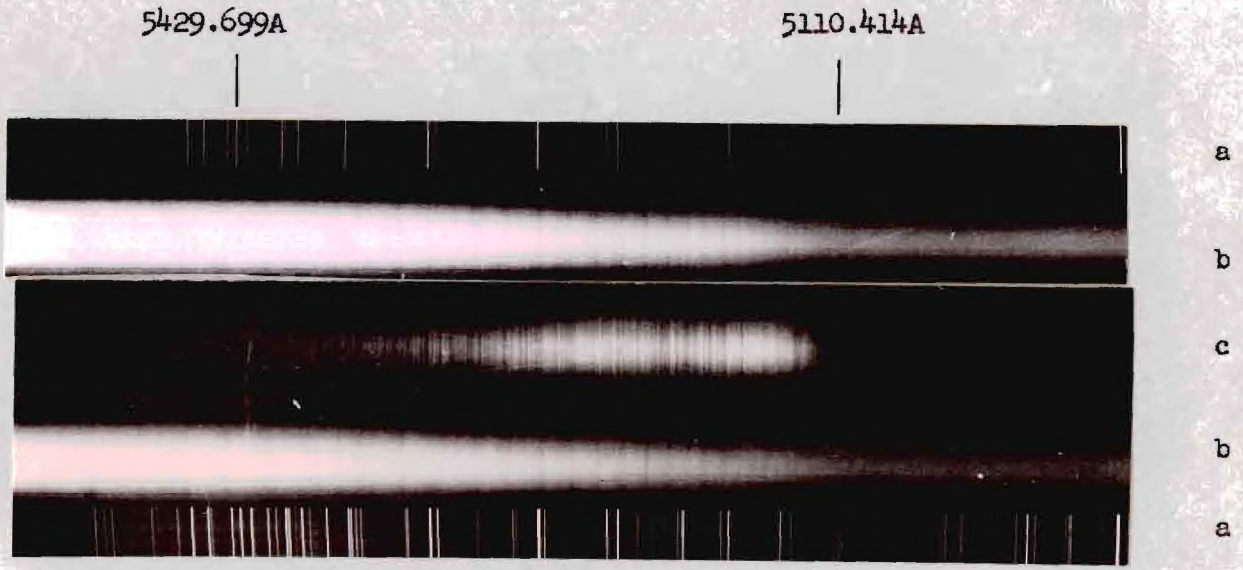


Figure 12

Magnetic Rotation Spectrum of $Br^{81}Br^{81}$

with a, b, and c same as in Figure 9.

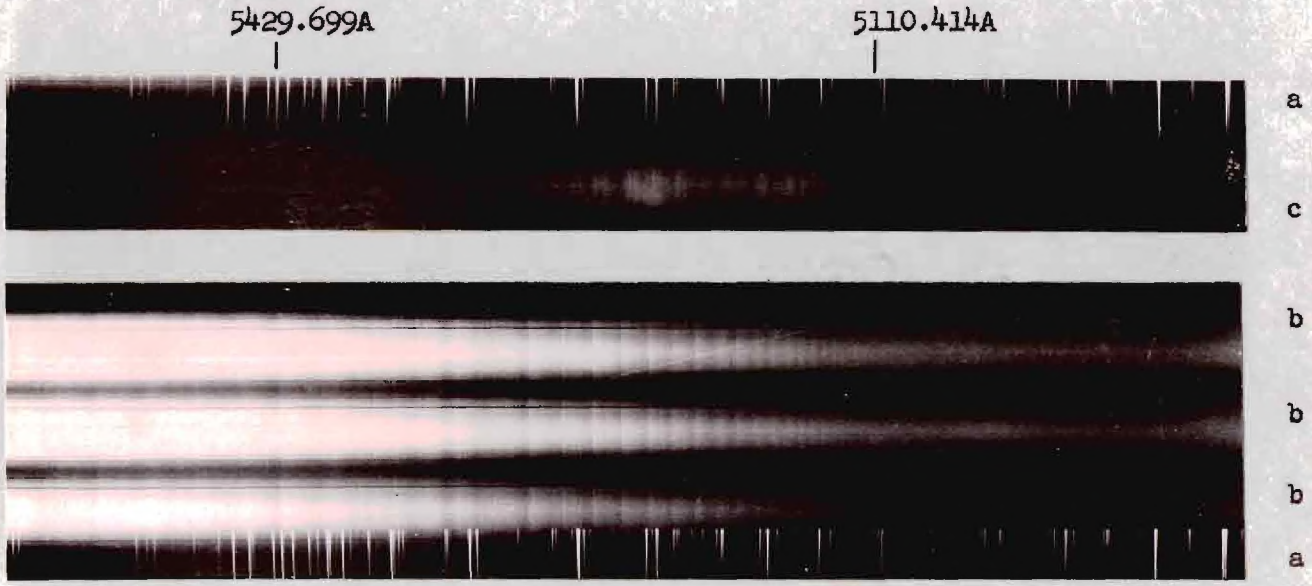


Figure 13

Magnetic Rotation Spectrum of $Br^{79}Br^{79}$

with a, b, and c same as in Figure 9.

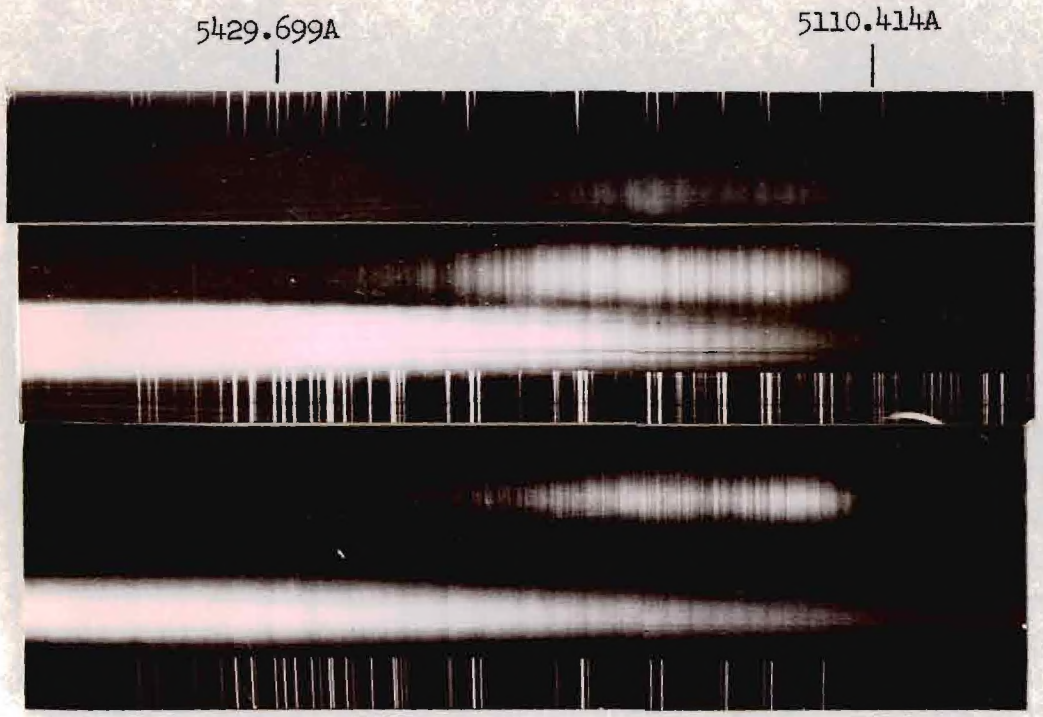


Figure 14

Magnetic Rotation Spectra of

$Br^{79}Br^{79}$, $Br^{81}Br^{81}$ and $Br_2$ with

a, b, c same as in Figure 9.

# CHAPTER VI

## CONCLUSION

Iodine monochloride was found to give a magnetic rotation spectrum between 5779A and 6682A. Most of its intense lines can be identified with the corresponding band origins in the absorption spectra of $ICl^{35}$ and $ICl^{37}$ for the $^3\Pi_1 \leftarrow {}^1\Sigma^+$ transition. Other lines may be due to perturbation of the upper state $^3\Pi_1$ with a repulsive state such as $0^-$ ($^3\Pi$). It was also found that $ICl^{35}$ predissociates at 5813.8A. Isotopic effects of ICl were measured for the v' progression from v = 9 to v' = 28 with v" = 0, and they agreed very well with the theoretical values.

Iodine monobromide gives a magnetic rotation spectrum of three bands between 5517A and 5710A for the $0^+ \leftarrow {}^1\Sigma^+$ transition. The magnetic rotation spectrum can be explained by assuming that the upper state $0^+$ is perturbed by a magnetically sensitive state such as $^1\Pi$ whose $W_e$ was found to be 33.7 $cm^{-1}$. The three bands are due to transitions from v" = 0, 1 and 2 to the points of perturbation. Each band consists of several lines due to $IBr^{79}$ and other lines due to $IBr^{81}$. Five pairs of lines of IBr can be identified with $IBr^{79}$ and $IBr^{81}$ correspondingly.

The magnetic rotation spectrum of bromine in the green region was well known but unexplained. It was found that the complexity of the spectrum is due to the overlap among the lines of $Br^{79}Br^{79}$, $Br^{79}Br^{81}$ and $Br^{81}Br^{81}$. With isotopically enriched $Br^{79}Br^{79}$ and $Br^{81}Br^{81}$, both the absorption and magnetic rotation spectra are much

simpler. The observed correlation between them indicates that the magnetic rotation spectrum of bromine is due to rotational distortion in analogy with the case of iodine.

No magnetic rotation spectra in the infrared region was found for IBr and $Br_2$.

Preliminary study on polyatomic molecules has been made. It was found that $NO_2$ gives a very intense magnetic rotation spectrum throughout the visible region. Due to the complexity of its absorption spectrum, the electronic transitions have not been analyzed and identified yet. A detailed analysis of its magnetic rotation spectrum may throw light on the identification of electronic transitions. Therefore, further study on $NO_2$ is highly recommended here. It was also found that $SO_2$ , $CS_2$ and HCHO are very promising for further study of their magnetic rotation spectra.

# APPENDIX I

## Derivation of the Equation for V for Hund's case (c)

Equation (13) in Serber's article (30):

$$V = 2CB \sum_{m''m'} \frac{\nu(n'n'')\,\nu^{(1)}(n'm';n''m'')\left[P_x(n''m'';n'm')P_y(n'm';n''m'')\right]}{\left[(\nu^2 - \nu(n'n)^2\right]^2} e^{-\frac{W_{n''}}{kT}}$$

We can derive for $^3\Pi_1 \leftarrow {}^1\Sigma$ of ICl (shown in Appendix 2)

$$^{(1)}(IJ'M';OJ''M'') = \frac{KM'}{hJ'(J'+1)}\mu_o \quad \text{where } K = \frac{-L(L+1)+S(S+1)+3Ja(Ja+1)}{2Ja(Ja+1)}$$

From Kronig's article:

$$\left[P_x(J,M;J-1,M\mp1)P_y(J-1,M\mp1;JM)\right] = \pm \frac{iP^2}{2}\frac{(J-1)(J\pm M)(J\pm M-1)}{J(2J-1)(2J+1)}$$

$$\left[P_x(J,M;J+1,M\mp1)P_y(J+1,M\mp1;JM)\right] = \pm \frac{iP^2}{2}\frac{(J+2)(J\mp M+2)(J\mp M+1)}{(J+1)(2J+1)(2J+3)}$$

$$\left[P_x(J,M;J,M\mp1)P_y(J,M\mp1;J,M)\right] = \pm \frac{iP^2}{2}\frac{(J\mp M+1)(J\pm M)}{J(J+1)}$$

$$P^2 = |P_x(^1\Sigma, {}^3\Pi_1)|^2$$

Final Results gives:

$$V = \frac{4\pi e \nu_1 P^2 \nu^2 B K e^{-\frac{W_J''}{kT}} f(J'')}{3hmc^2(\nu^2 - \nu_1^2)^2}$$

where $f(J'') = \frac{J''+2}{J''+1}$ for R branch

APPENDIX I
(Continued)

$$f(J'') = -\frac{J''-1}{J''} \quad \text{for P branch}$$

$$f(J'') = \frac{2J''+1}{J''(J''+1)} \quad \text{for Q branch}$$

$$\nu_1 = \nu_1({}^3\pi, {}^1\Sigma)$$

$$B = \frac{N}{\sum_n e^{-\frac{W_a}{kT}}}$$

# APPENDIX 2

## Zeeman Effect in Band Spectra of Diatomic Molecules with Case (c) Coupling

With the notations according to Herzberg (52) and with $\mu$ as the magnetic moment, we have

$$\mu_L = \sqrt{L(L+1)}\,\mu_o \; ; \qquad \mu_S = 2\sqrt{S(S+1)}\,\mu_o \; ;$$

$$\mu_{Ja} = \mu_L(\cos L\cdot Ja) \; + \; \mu_S(\cos S\cdot Ja);$$

$$\mu_\Omega = \mu_{Ja}(\cos Ja\cdot \Omega); \; \mu_J = \mu_\Omega(\cos\Omega\cdot J); \text{ and}$$

$$\mu_H = \mu_J(\cos J\cdot H).$$

From Figure 104 (52), we get, by the Law of cosines and by trignometrical relations,

$$S(S+1) = L(L+1) + J_a(J_a+1) - 2\sqrt{L(L+1)}\sqrt{J_a(J_a+1)}\;\cos(L\cdot J_a);$$

$$L(L+1) = S(S+1) + J_a(J_a+1) - 2\sqrt{S(S+1)}\,\sqrt{J_a(J_a+1)}\,\cos(S\cdot J_a);$$

$$\cos\Omega\cdot J_a = \frac{\Omega}{\sqrt{J_a(J_a+1)}};$$

$$\cos\Omega\cdot J = \frac{\Omega}{\sqrt{J(J+1)}} \; ; \text{ and}$$

$$\cos J\cdot H = \frac{M}{\sqrt{J(J+1)}}.$$

# APPENDIX 2

## Zeeman Effect in Band Spectra of Diatomic Molecules with Case (c) Coupling (Continued)

By substituting these expression for the cosines into the above formulas for magnetic moments, we get the final result as follows:

$$\mu_H = \frac{-L(L+1)+S(S+1)+3J_a(J_a+1)}{2Ja(Ja+1)} \left(\frac{M\,\Omega^2}{J(J+1)}\right) \mu_o$$

by letting $K = \frac{-L(L+1)+S(S+1)+3Ja(Ja+1)}{2Ja(Ja+1)}$,

we have $\mu_H = K\left(\frac{M\,\Omega^2}{J(J+1)}\right)\mu_o$.

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# VITA

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